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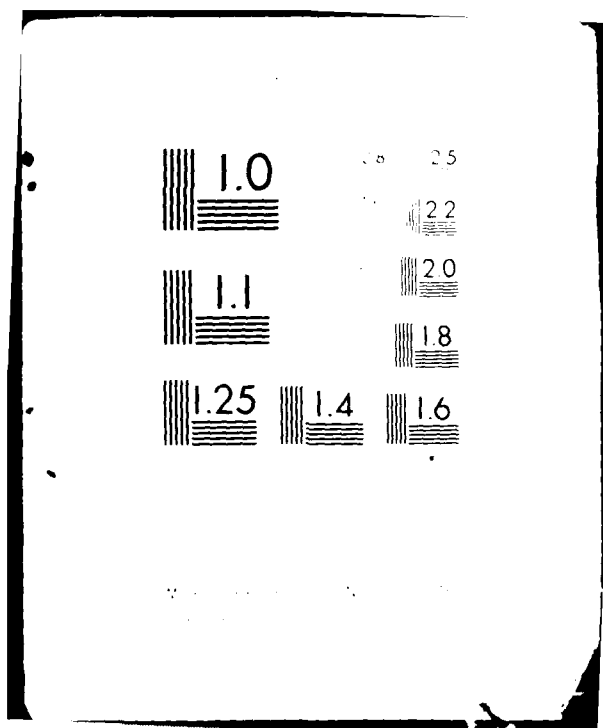
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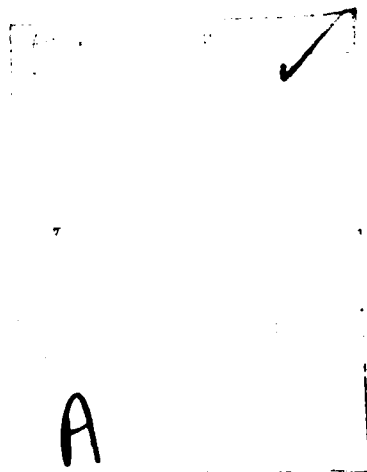
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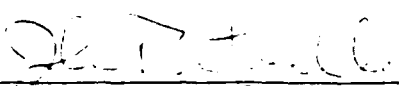
A Trident Scholar Project Report


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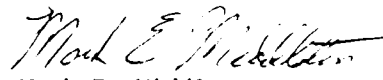
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Mark E. Middleton

4 May 1981

Annapolis, Maryland



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## 1. INTRODUCTION

As a basis for experiment, there exists a need for standards that can be used as references. The triple-point of water serves as a good example of a reference for temperature. Since water exists as a gas, liquid, and solid at only one precise temperature, it can be used as a reference in any laboratory. While good references for absolute pressure have been developed via dead weight testers, suitable transfer (or secondary) standards for pressure do not yet exist in the 0.1 - 0.5 GPa region. Therefore, it was decided to investigate the phase change of a plastic crystal as a possible transfer standard.

The basic idea is to use a capacitor to measure the dielectric constant of a plastic crystal as a function of pressure and thereby observe the phase transition. In order to serve as a good reference point, a transition from one state to another must obey three conditions:

- (1) The transition must be reproducible under all laboratory conditions.
- (2) The change in the dielectric constant as a result of a transition must be sharp. That is to say, the rate of change of the dielectric constant must be great at the transition pressure, but it must be small at surrounding pressures.
- (3) The transition pressure must have little temperature dependence.

If these three conditions are met in a plastic crystal, then it could be used as a pressure reference point.

## II. PLASTIC CRYSTALS

### A. A General Description

The title of "plastic crystal" is given to any compound which enters a soft, waxy solid phase in which the molecules are orientationally disordered. That is to say, a plastic crystal has a normal solid phase in which the molecules occupy their normal lattice positions but do not have the same orientations. In most respects, a plastic crystal undergoes the same phase changes that a normal crystal would. It is only set apart by its unique plastic phase. This plastic phase is known also as the rotator phase since several of the molecules have rotated to random orientations.

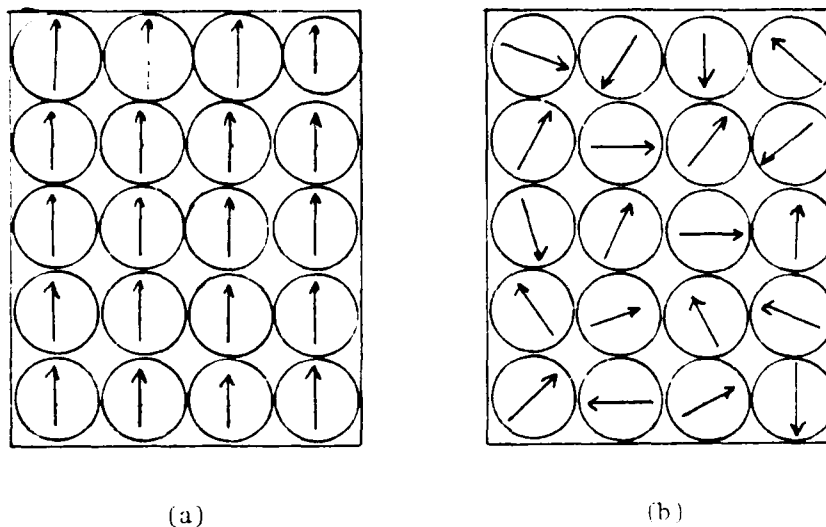


Figure 1: A two dimensional lattice with a molecule at each lattice position; (a) The non-rotator solid phase in which the molecules are oriented in the same direction; (b) The rotator phase in which the orientation of the molecules is random.

The rotator phase of a plastic crystal occurs when the volume increases to the point where the barrier to molecular rotation can be breached. This does not mean that each molecule is completely free to rotate. But with a reasonable amount of energy, a molecule can overcome the resistive forces from the molecular bonds and line up in a different direction. Since the crystal bonds have not been broken, the crystal still maintains its lattice structure.

#### B. Carbon Tetrachloride

Carbon tetrachloride is a plastic crystal which has been studied extensively using several experimental techniques. At present, there is a good understanding of the phases observed in  $\text{CCl}_4$ . The phase diagram reported by Bridgman<sup>1</sup> in Figure 2, displays the relationships of the phases with respect to temperature and pressure. The region belonging to the rotator phase is called the Ib phase. X-ray diffraction has determined the Ib phase to have a rhombohedral lattice structure. The most common non-rotator phase is phase II. This phase has a monoclinic lattice structure.

The phase diagram published by Bridgman was not complete, however. Further experimentation revealed the existence of a second rotator phase in the same region as the rhombohedral phase. Named the Ia phase, it is determined to be a face-centered cubic lattice with a greater molecular volume than the Ib phase. The Ia phase was difficult to discover because it actually exists at a lower temperature than the Ib phase. Consequently, the liquid should transform into the Ib phase at the transition temperature and

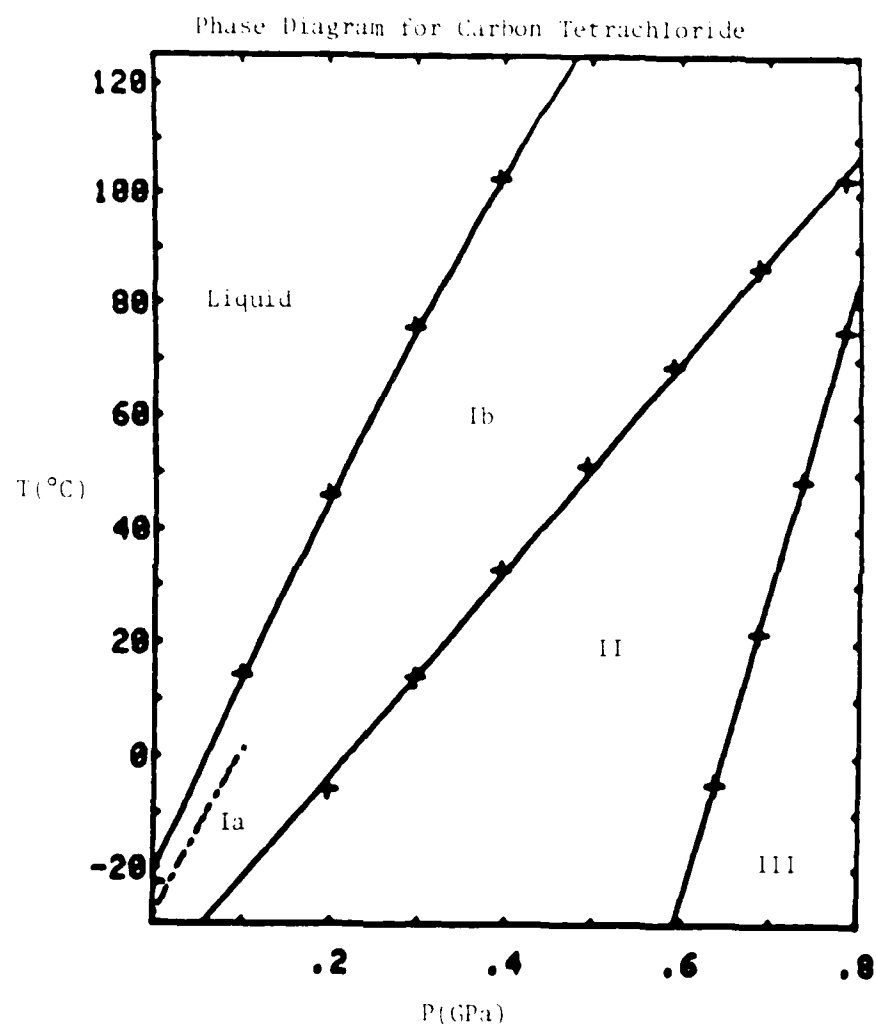


Figure 2: The phase diagram of carbon tetrachloride as reported by Bridgman<sup>1</sup>. The Ib phase is the rhombohedral phase. The II phase is the monoclinic phase. The III phase is orthorhombic. The Ia phase, not reported by Bridgman, is face-centered cubic.

never reach the Ia phase. But since carbon tetrachloride exhibits the ability to supercool, the Ia phase can be entered with cautious experimental technique. It is possible to transform from the Ia phase into the Ib, but the reverse is not true. The Ia phase is metastable since it can enter the Ib phase at any time.

Recently, work has been done by Bean and Wood<sup>2</sup> using differential thermal analysis (DTA) to determine the monoclinic, rhombohedral, face-centered cubic, and liquid phase diagram. Their work is pictured in Figure 3. In conjunction with Bean's DTA work, this paper will discuss the first dielectric measurements reported on the liquid to rotator and rotator to liquid phase transitions of carbon tetrachloride.

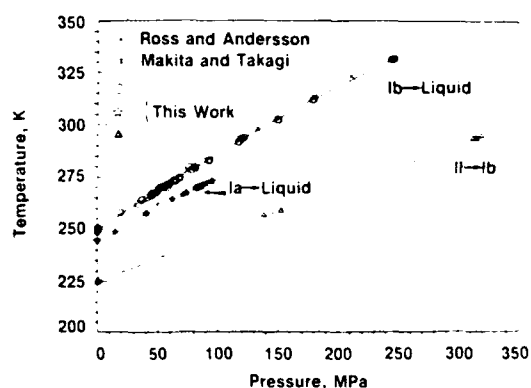


Figure 5: The Ia-Liquid, Ib-Liquid, and II-Ib curves reported by Bean<sup>2</sup> using DTA.

Dielectric data on the liquid phase of  $\text{CCl}_4$  has been reported by Scaife<sup>3</sup> and Mopsik<sup>4</sup>. The two are in agreement that the Clausius-Mossotti equation fits  $\text{CCl}_4$  with a linear approximation for density. Their work stops short of the phase transition, however. Since  $\text{CCl}_4$  has no permanent dipole moment, the dielectric constant should depend primarily on the density of  $\text{CCl}_4$ . To conduct the necessary experiment, two separate cells have been built. Both cells collect dielectric data as a function of pressure.

#### C. Cyclohexane and Cyclohexanol

After carbon tetrachloride was studied, a search was instituted for another crystal that could be used for pressure calibration. From the atmospheric pressure melting point, it was determined that cyclohexane should have a phase transition at about the right pressure. Cyclohexane has the additional advantage that it has a face-centered cubic lattice, so that the dielectric results do not depend on the orientation of the crystal.

Since both  $\text{CCl}_4$  and cyclohexane are non-polar, it was decided to also investigate a polar fluid. Cyclohexanol was chosen because of the possibility of an appropriate pressure-induced phase transition. The additional advantage is that the dipole moment in the rotator phase should actually cause the molecules to rotate in an alternating electric field, and have a very large dielectric constant. In the non-rotator phase the dielectric constant should be very low since the dipoles can't line up with the field. Thus, the rotator-nonrotator phase transition should be easily observable and hence should be studied for use in pressure calibration.



### III. DIELECTRIC ANALYSIS

#### A. Dielectric Theory

Dielectric analysis relies on the principle that any material present in an electric field tends to change that field. Furthermore, it assumes that the electric field changes as a direct result of changes in the configuration and density of that material. To assist with experimental measurement, a physical variable known as the dielectric constant is introduced. The dielectric constant is the ratio of the electric field strength in vacuum to that in the material for the same distribution of charge on two conductors. The dielectric constant is also known as permittivity.

Capacitors represent the most efficient way of measuring a dielectric constant. A capacitor with a charge  $Q$  on the conductors and a potential  $V$  between them is said to have a capacity.

$$C = \frac{Q}{V} \quad (1)$$

Consider a simple parallel plate capacitor in free space, as in Figure 4a. From equation (1) and Coulomb's Law, the capacity of the parallel plates is:

$$C_o = \frac{\epsilon_o A}{d} \quad (2)$$

where  $A$  is the area of the plates  $d$  is the separation between them and  $\epsilon_o$  is the permittivity of free space. Now suppose that a material, known as a dielectric is introduced between the plates and completely fills the spaces there, as in Figure 4b.

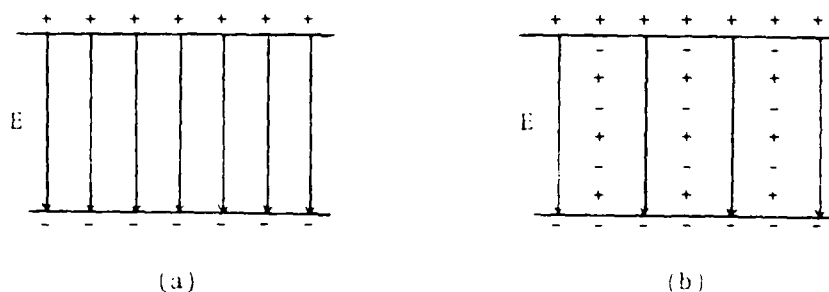


Figure 4: (a) Capacitor in vacuum; (b) Capacitor filled with a dielectric. (From V.V. Daniel in Dielectric Relaxation, New York: Academic Press, Inc., 1967 p. 14.)

As an electric field is applied, the negative charges in the dielectric move slightly towards the positive plate and the positive charges move slightly toward the negative plate. Consequently, the field strength and potential across the plates are reduced by a factor equal to the permittivity of the material. Through the decrease in potential in equation (1), the capacitance increases. Therefore, the dielectric constant of a material can be measured as the ratio of the capacitance with the material present to that in a vacuum.

$$\epsilon' = \frac{C}{C_0} \quad (3)$$

#### B. Clausius-Mossotti Equation

By filling the spaces of a capacitor with a dielectric, the capacitance increases. If the density of that dielectric increases, the added molecules further increase the capacitance. The relationship between density and permittivity is known as the Clausius-Mossotti equation, which is presented here without proof;<sup>5</sup>

$$\frac{(\epsilon' - 1)M}{(\epsilon' + 2)\rho} = \frac{4\pi N\alpha}{3} \quad (4)$$

where  $\rho$  is the density of the dielectric,  $M$  is the molecular weight of the dielectric,  $N$  is Avogadro's number, and  $\alpha$  is the molecular polarizability. Molecular polarizability is the ability for a molecule to polarize in an electric field. In carbon tetrachloride, molecular polarizability is a measure of the ability to form an induced dipole moment since no permanent dipole exists. Recent studies have shown that the molecular polarizability is not actually a constant, but varies linearly with density<sup>3,4</sup>. The change is so small, however, that it can be treated as a constant.

Consequently, the Clausius-Mossotti equation implies that changes in the permittivity of a material with pressure are dominated by the density. Therefore, dielectric analysis becomes a means of determining the density of a dielectric.

The Clausius-Mossotti equation also provides a means for calculating the compressibility of a substance. Compressibility is defined as the rate of change in unit volume with respect to pressure and is shown as

$$\kappa = - \frac{1}{V} \left( \frac{dV}{dP} \right) \quad (5)$$

By substituting into the Clausius-Mossotti equation  $V = (M/\rho)$  and taking the derivative with respect to pressure, an expression for compressibility can be determined,

$$\frac{(\epsilon' + 2) - (\epsilon' - 1)}{(\epsilon' + 2)} \left( \frac{d\epsilon'}{dP} \right) = - \frac{1}{V} \frac{4\pi N\alpha}{3} \left( \frac{dV}{dP} \right) + \frac{4\pi N}{3V} \left( \frac{d\alpha}{dP} \right)$$

$$\frac{3}{(\epsilon' - 1)(\epsilon' + 2)} \left( \frac{d\epsilon'}{dP} \right) = - \frac{1}{V} \left( \frac{dV}{dP} \right) + \frac{1}{\alpha} \left( \frac{d\alpha}{dP} \right)$$

$$\kappa = \frac{3}{(\epsilon' - 1)(\epsilon' + 2)} \left( \frac{d\epsilon'}{dP} \right) - \frac{1}{\alpha} \left( \frac{d\alpha}{dP} \right)$$

The term  $(1/\alpha)(d\alpha/dP)$  is the rate of change of the molecular polarizability with respect to pressure. For liquids, this term can be treated as a constant to within 5% error. For the purposes of the present report, it will be assumed to be the same in the solid phase as in the liquid. This assumption is currently being checked since careful density measurements on solid  $\text{CCl}_4$  at the National Bureau of Standards (NBS) are being made. Since  $\alpha$  consists only of the polarization of the electron relative to the nucleus, however, it is felt that the  $(1/\alpha)(d\alpha/dP)$  term should be approximately constant and independent of whether  $\text{CCl}_4$  is a solid or liquid. From measurements reported by Scaife<sup>3</sup>, the error can be calculated,

$$\frac{1}{\alpha} \left( \frac{d\alpha}{dP} \right) = - 0.0539 \text{ (GPa}^{-1}\text{)}$$

Therefore, the final expression for compressibility is

$$\kappa = \frac{3}{(\epsilon' - 1)(\epsilon' + 2)} \left( \frac{d\epsilon'}{dP} \right) + 0.0539 \text{ (GPa}^{-1}\text{)} \quad (6)$$

#### IV. EXPERIMENTAL DESIGN

The high pressure data were obtained using a sample cell adapted to commercial high pressure equipment. The sample cell pictured in Figure 6. makes use of the three terminal cylindrical capacitor design concept. Constructed entirely of brass, the inner electrode of the cylindrical capacitor is divided into three sections. The two end sections are connected to a center support and are grounded. The middle section is held in place by the center support and is insulated from the ground by use of mylar and epoxy. The middle section is connected to the low terminal by means of an insulated wire run through, and shielded by, the center support. The outer electrode is held in place by insulating rings made of phenolic and is connected to the high terminal by a short wire. In this way, only the middle portion of the capacitor is measured and fringe effects are eliminated.

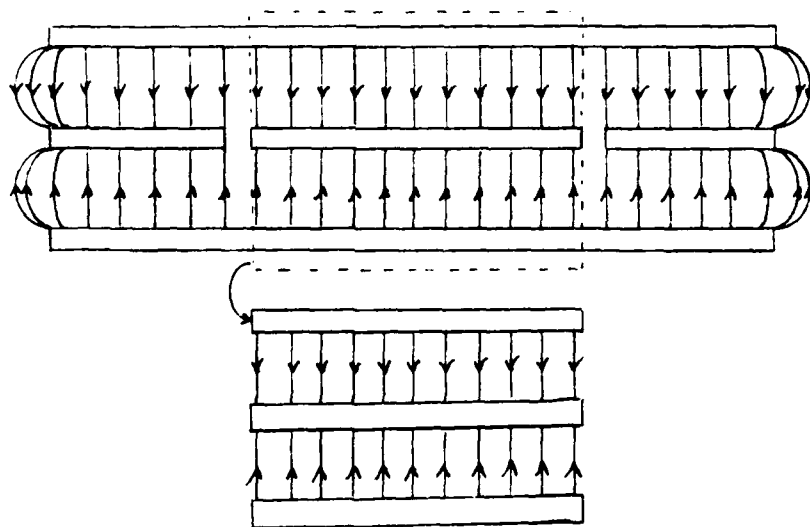
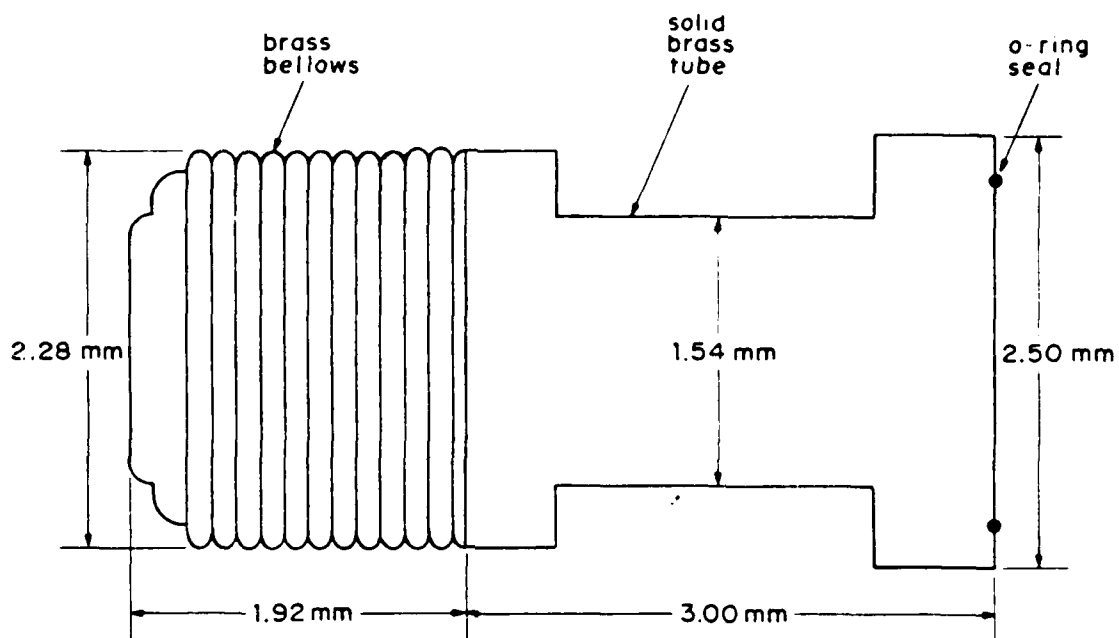


Figure 5: Cylindrical three terminal capacitor used to measure permittivity.

## The Sample Cover



## The Sample Cell

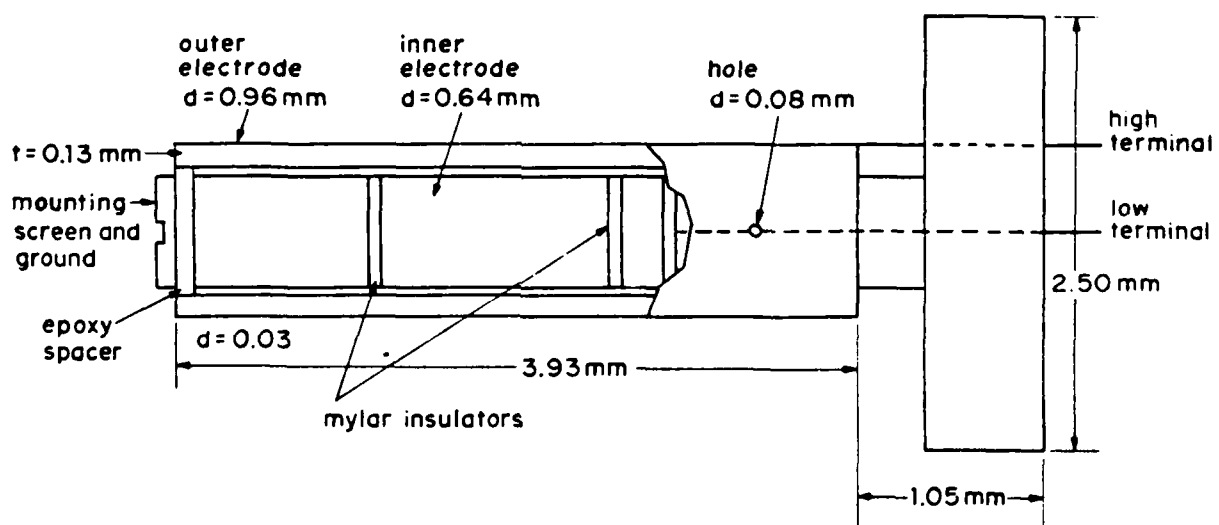


Figure 6: The sample cell

To allow the pressure to be felt inside the capacitor, twelve small holes were drilled in the outer electrode. Additional dielectric is allowed to flow into and out of the capacitor to equalize pressure, but the effect on capacitance from the holes is negligible. In this way the capacitor becomes a constant volume capacitor with essentially no corrections to determine the dielectric constant. The cylindrical capacitor is shielded from the hydraulic pressure fluid by a solid brass tube with a bellows attached to the end. This cover also allows for a reservoir of approximately 5.5 ml of dielectric available to fill the capacitor.

Fully assembled, the cell is mounted in a commercial pressure bomb rated to 200,000 psi. A small hand pump was used to pump the pressure of the bomb to a maximum of 50,000 psi. The pressure bomb itself is immersed in a temperature bath of ethylene-glycol. The temperature was controlled by a proportional control unit and the temperature was measured using a digital quartz thermometer. The temperature of the bath was constant to within  $\pm 0.2^\circ\text{K}$  of the stated value. The pressure of the bomb was first measured using a calcium fluoride capacitor described by Andeen<sup>6</sup>. After several experimental runs, a bourdon tube gage was substituted for the calcium fluoride capacitor with little loss of accuracy. The accuracy of the pressure measurements are  $\pm 10^{-3}$  GPa.

The capacitance of the cell was measured using a capacitance bridge designed by Carl Andeen and described in appendix II. The accuracy of the capacitance readings is  $10^{-5}$  pico-farads. To determine whether the sample cell needed capacitance corrections

as a function of pressure, a calibration run was conducted with argon gas used as the dielectric medium. The results, reported in Figure 28., coincide within experimental error with the published values of argon gas under pressure. While no pressure dependence was observed, a slight temperature dependence of  $2 \times 10^{-3} \text{ pF/K}$  was detected in the cell. Use of a zero pressure capacitance at each temperature eliminated the effect due to temperature.

The carbon tetrachloride was obtained from two sources. Eastman Kodak Spectro ACS  $\text{CCl}_4$  obtained at NBS was studied as well as Fisher Chemical Co. brand obtained at the USNA chemistry stores. The samples of cyclohexane were obtained at USNA and were Fisher brand. The cyclohexane was studied both before and after fractional distillation. The cyclohexanol was produced by the Aldrich Chemical Co. and was obtained at USNA.

The initial experimental design also included a thermocouple to collect DTA data. After a few data sets were taken, it was apparent that the DTA data was yielding no additional information to the dielectric data. Therefore, the DTA work was discontinued.



## V. RESULTS

The rotator phase was entered at a total of twelve temperatures to insure that a broad temperature range was covered. The six most representative temperatures are displayed in Figures 10-15. in Appendix I. The data runs at 21.0°C, 14.3°C, 11.5°C, and 1.9°C were obtained using Fisher Chemical Co. brand CCl<sub>4</sub> and the runs at -6.0°C and -13.4°C were obtained using Eastman Kodak Co. brand CCl<sub>4</sub>. To convert the capacitance readings into permittivity, the zero pressure permittivity was calculated from CRC's Handbook of Physics and Chemistry and was confirmed by Scaife<sup>3</sup> and Mopsik<sup>4</sup>. Next, a zero pressure vacuum capacitance was calculated using equation (7).

$$C_0 = \frac{C}{\epsilon'} \quad (7)$$

The capacitance readings from the raw data were then converted to relative permittivity values using equation (5). The zero pressure permittivity and vacuum capacitance values are reported in Table 1.

T(°C)	21.0	14.3	11.5	1.9	-6.0	-13.4
$\epsilon'$	2.2366	2.2500	2.2556	2.2748	2.2906	2.3054
C (pF)	3.7916	3.7867	3.7921	3.7885	3.7847	3.7849

Table 1: Computed relative permittivities and zero pressure vacuum capacitance values used to calculate permittivity in Figures 10 -15.

The cyclohexane data was taken at three different temperatures and a typical curve at 35.5°C is included in Figure 25. in Appendix I. The two curves displayed represent the negligible effects due to differences in purity. Qualitative data were only taken at

-10.0°C for cyclohexanol. These results are plotted in Figure 24. Since no quantitative fit was made with cyclohexane and cyclohexanol, the capacitive values were not changed into permittivity. The curves are important for their qualitative aspects and will be discussed further.

## VI. DISCUSSION OF RESULTS

### A. The Liquid Phase

The liquid phase of carbon tetrachloride has previously been studied as a function of pressure by both Scaife<sup>2</sup> and Mopsik<sup>3</sup>. In their papers they report data in the 25°C - 50°C region and fit their data to the Clausius-Mossotti equation. The experimental design of the sample cell in this paper does not allow for density measurements, but yields permittivity only as a function of pressure. It was found that the permittivity can be fit to a quadratic expression of pressure within experimental error. The coefficients for equation (8) are reported in Table 2. below.

$$\epsilon' = \epsilon_0 + aP + bP^2 \quad (8)$$

In order to compare the results of the present work with that of Scaife and Mopsik, their data were also fit to equation (8) and the results are included in Table 2. The data presented in this paper are in fairly good agreement with the results of those workers. The present method of analysis points out an interesting trend. It is seen that in all cases, the standard error increases as temperature increases. This implies that equation (8) becomes less valid as temperature increases. That is, higher order terms should be added to equation (8) as temperature increases. It will be of interest to investigate the reason that higher order terms become more important as temperature increases.

T(°C)	a	a(GPa <sup>-1</sup> )	b(GPa <sup>-1</sup> )	STD ERROR
21.0	2.2377	1.4626	-2.7326	8.473E-4
14.3	2.2536	1.3367	-2.6195	5.131E-4
11.5	2.2563	1.3392	-2.8469	5.459E-4
1.9	2.2750	1.4176	-3.4154	1.809E-4
-6.0	2.2912	1.3048	-3.4079	2.426E-4
-13.4	2.3056	1.1935	-2.8044	0.708E-4
53.9 <sup>3</sup>	2.1825	1.8353	-4.4249	12.909E-4
25.0 <sup>3</sup>	2.2323	1.5742	-3.3418	7.610E-4
50.0 <sup>4</sup>	2.1823	1.6259	-2.6616	23.594E-4
25.0 <sup>4</sup>	2.2294	1.5594	-3.2251	7.603E-4
0.0 <sup>4</sup>	2.2784	1.4287	-3.4081	1.108E-4

Table 2: Coefficients for use in equation (3).

#### B. Superpressing

In every set of data acquired by pressing the liquid into the rotator phase, there was a fair amount of overpressing before the liquid transformed. This overpressing is known as superpressing and is analogous to supercooling. Consider a liquid which is being cooled to the temperature where it will change into a solid. If that liquid does not transform, but continues to cool below the transition temperature, the liquid is said to be supercooled. In much the same way, carbon tetrachloride can be pressed above its phase transformation pressure. Figure 7. shows an excellent example of carbon tetrachloride in the superpressed region.

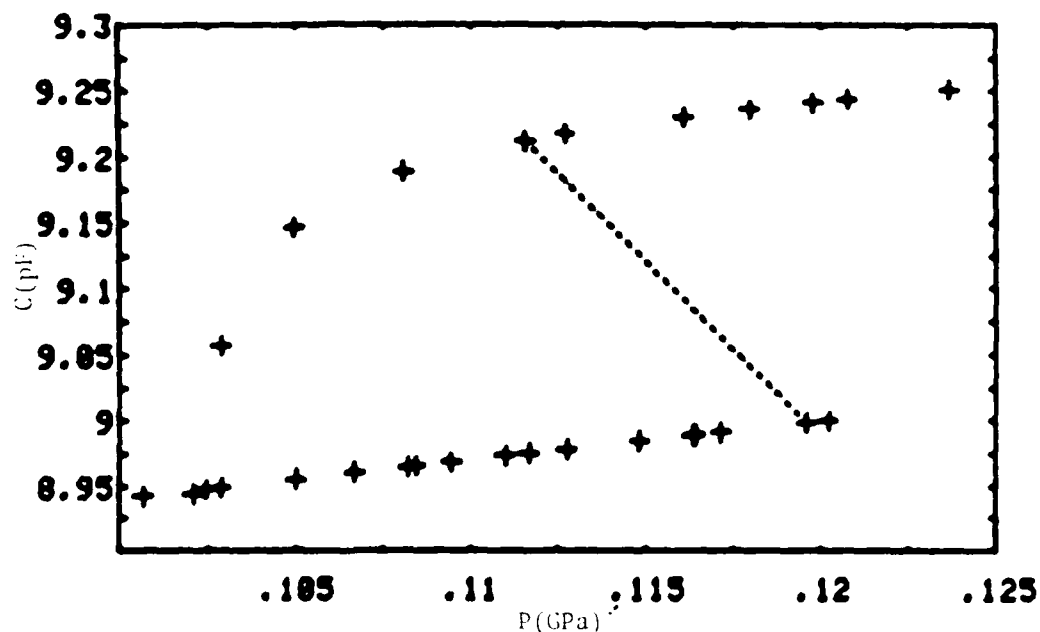


Figure 7: The superpressed region of carbon tetrachloride at a temperature of 14.3°C. The dotted line represents a jump from the superpressed region into solid  $\text{CCl}_4$ . The point at a pressure greater than the transition point was taken on a previous run that did not transform.

The superpressed state of carbon tetrachloride is metastable since it should be in a different phase under the same physical conditions and can be transformed by a simple shock wave caused by rapping the bomb with a pencil or by a sudden pressure increase. As the degree of pressurization increases, it becomes easier for a shock wave to cause a phase change. Next, there appears to be a maximum pressure to the superpressed state. Pressures above this maximum cannot be reached without a phase transition.

Finally, it is found that the width of the superpressed

region decreases as temperature increases. There seems to be some thermal dependence in superpressing which allows lower temperatures to superpress for wider pressures. This is not unreasonable.

The superpressed region of carbon tetrachloride was studied extensively to determine if the region had any unusual characteristics of its own. Using the coefficients reported in Table 2., the liquid curves were fitted into the superpressed region with a great degree of accuracy. There are no anomalies associated with the superpressed region. It appears to be a mere extension of the normal liquid phase.

#### C. Liquid to Rhombohedral Phase Transition

Although the phase transition could not be predicted, the actual transitions were easily observed. The transition was characterized by a decrease in pressure in addition to a jump in permittivity. The dotted line in Figure 7. indicates the jump from liquid to solid. The decrease in pressure is the result of a sudden decrease in volume of the sample. To keep constant pressure, additional pressure fluid must be placed into the bomb to fill the space vacated by the carbon tetrachloride. Without additional fluid, the space must be filled up by a decrease in density of the fluid present, and hence, the pressure decreases.

Once the carbon tetrachloride transforms into the solid phase, however, there is no evidence of hysteresis as shown by Figure 7. The figure shows points for both increasing and decreasing

pressures. The curve is very well defined, and unlike the liquid to solid transition, the solid to liquid transition has a well defined melting point. Figure 25, included in Appendix I is a plot of the melting transition points for the different data sets.

#### D. The Rhombohedral Phase

The rotator phase of carbon tetrachloride is distinguishable by its higher values of permittivity. These higher values are predicted by the Clausius-Mossotti equation because the rhombohedral phase is more dense than the liquid phase. The initial jump in permittivity is caused by the sudden change in volume during the phase transition. After the jump to the solid phase, upon decrease of pressure, the volume increases (density decreases) gradually until the sample melts. Upon increase of pressure after the jump to the solid phase, the volume decreases (density increases) gradually until a region characteristic of normal solids is reached. Consequently the melting of  $\text{CCl}_4$  exhibits a diffuse nature.

At first, it was difficult to believe that the diffuse effect was real. Specifically, it was felt that there was incomplete melting in the cell because of geometrical limitations. It is possible that there is a pressure gradient in the sample cell which would vary the pressure in the cell, allowing liquid in one region and solid in another. In this case, it would be expected that time effects would be observed while pressure equilibrates. No changes in capacitance were observed as a function of time. Also, a second cell consisting of two parallel plates was constructed and pressurized under the same conditions

as previous sample runs. The results indicate the same diffuse region in the second cell as in the first. This result implies that the geometry of the cell is not responsible for the diffuse region.

Upon learning of these results, Bean designed a cell in which density readings were taken as a function of pressure. His results indicate the same diffuse nature of the curve, which implies that it is not a result of squeezing the sample into the constant volume capacitor. Thus the rounding of the melting curve is an intrinsic property of carbon tetrachloride. There are several possible explanations for this effect.

1. Solid-Liquid Coexistence

It is still possible that both solid and liquid carbon tetrachloride might coexist together, despite the lack of a pressure gradient. Nevertheless, it is difficult to understand how solid and liquid can mutually coexist over a wide range of pressure.

2. Impurity Effects

A second possibility is that the sample impurity was responsible for the broad diffuse region. As a check on the effect of sample purity,  $\text{CCl}_4$  from two different sources were studied. Identical results were obtained, suggesting that impurities were not responsible for the effect. However, the experimentation with cyclohexane was much better evidence that sample purity is not the cause of the diffuse region. Figure 23. displays two curves



of cyclohexane at 35.0°C. One curve represents a sample of impure cyclohexane and the other curve represents pure cyclohexane. The impure curve was obtained with cyclohexane originating from the USNA chemistry store. The sample purity was checked by trying to grow cyclohexane crystals. The sample was so impure that a single crystal could not be obtained. Dr. Alan Chadwick of Kent University proceeded to fractionally distill the cyclohexane until a single crystal with no optical defects was grown. That liquid was then placed in the sample cell and new data was taken.

In addition to no discernible differences between the two curves, both curves had evidence of the same diffuse nature which was observed in carbon tetrachloride. This would indicate that sample purity was not a factor.

### 3. Highly Defective Crystal

The diffuse region in cyclohexane could also indicate a highly defective crystal structure. A common example of a defect is a Schottky defect in which an ion occupying a lattice point gains enough energy to jump from its lattice point and attach itself to the surface of the crystal. Since the rotator phase is characterized by a low potential barrier to rotation, it is possible that the energy to move a molecule from a lattice point to the surface is also low. Consider the crystal lattice as pressure is decreased. In the high pressure region where no transition effects are observed, the crystal is virtually free from defects as in Figure 8a. As the pressure is decreased, enough energy becomes available for a few molecules to jump to the surface

as in Figure 8b. Close to the transition point, the number of defects grows exponentially. Enough energy is available that the crystal becomes highly defective with a density close to that of the liquid. This state is pictured in Figure 8c. Finally, the probability of defects becomes so great that there are not enough regular lattice points occupied to keep the lattice structure. This is when the crystal becomes a liquid.

This theory might also explain why the rhombohedral to monoclinic (Ib-II) transition is so well defined. Since the crystal is highly ordered when entering the phase transition, a simple reordering of the structure is required to take place. No defects need to be replaced so the transition would be sharp.

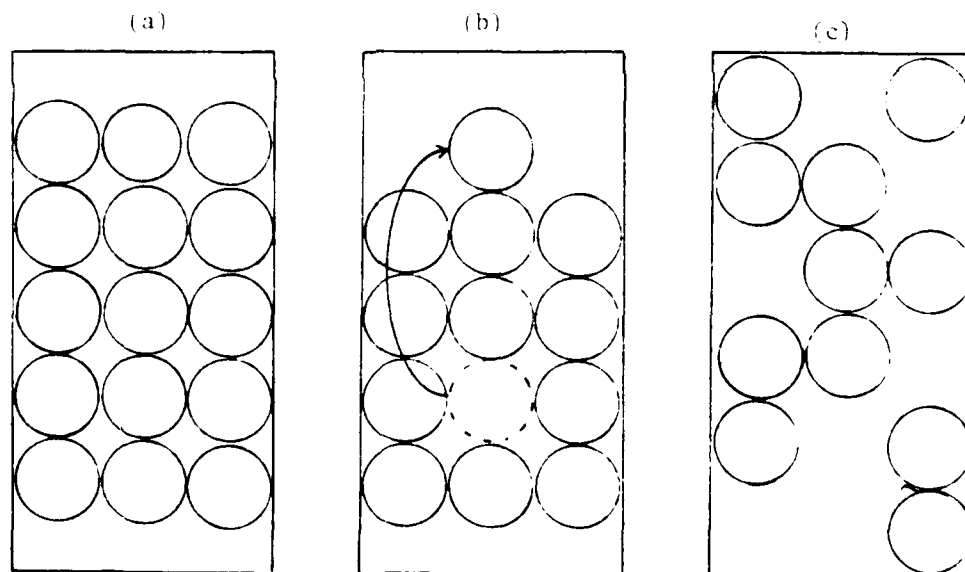


Figure 8. (a) A perfect crystal lattice under high pressure.  
 (b) A Schottky-type defect where a molecule jumps to the surface.  
 (c) The highly defective state of the crystal.

#### 4. Elastic Lattice Spacings

A fourth possibility for the diffuse nature of the melting in the rotator phase is that it is merely a lattice expansion effect due to the nature of the interatomic potentials. Consider carbon tetrachloride that has just transformed from liquid to solid. The  $\text{CCl}_4$  occupies a complete lattice, but the interatomic force is very weak. Under these conditions, a small change in pressure provides enough force to overcome the particle-particle repulsive potential, and large changes in volume are apparent. As the crystal is placed under increasing pressure, the lattice spacings become smaller and the repulsive potential becomes stronger. This increase in repulsive potential causes larger amounts of pressure to be required to change the volume of  $\text{CCl}_4$ . That is to say, the volume changes less with each successive increase in pressure. Finally, the changes in volume become so small, that they become more "normal".

Although experiments have been conducted to determine the lattice spacings of the Ib phase, none was done under pressure, and none was done in the diffuse region. This suggests a possible experiment to be done with x-ray diffraction techniques to determine if the spacings do actually change in the diffuse region.

#### E. Compressibility of $\text{CCl}_4$

Compressibility has been described previously in Sec III.B and can be calculated using equation (6). The rate of change of  $\epsilon'$  with respect to pressure was easily calculated from equation (8). The solid change was more difficult to fit. Nevertheless, a spline fit between successive sets of four points was used to predict the change in permittivity for the middle two points. Using equation (6), the curves in Figures 16.-22. were generated.

Three features are particularly interesting. First, the compressibility of the solid phase beyond the rounded region of the melting curve is about the same as that of the liquid. That is to say, the curves for the liquid region and higher pressure solid region appear to form one continuous curve. The points falling below the transition region which link the solid curve with the liquid curve are from the superpressed region. Again this indicates that the superpressed region is merely an extension of the liquid phase.

Second, the compressibility becomes quite large just before melting. In fact, the singularity in the compressibility is reminiscent of the specific heat during  $\lambda$  transitions for example. Certainly, this represents important information concerning this phase transition. Further work is necessary, however, before the full implications can be realized.

Finally, for the liquid the compressibility curve is not quite linear, but curves slightly upward. This is reasonable in that it shows that the liquid becomes less compressible the more it is compressed.

### F. Face-centered Cubic Ia Phase

In over fifty attempts to freeze into the Ia face-centered cubic phase in either constant volume cell, not one attempt was successful. However, rough capacitance measurements were performed at USNA in the NBS cell used for the DTA measurements of Bean and Wood<sup>2</sup>. That cell immediately yielded the Ia phase on the first pressurization. That the Ia phase was obtained was determined by the melting pressure of that solid. Furthermore, the melting was found to be diffuse for that phase as well. The NBS cell was pressurized again and the Ia phase was obtained. In this instance the pressure was increased further, and after a few thousand psi was added, the Ia phase transformed into the Ib phase. The capacitance for the Ia phase was about halfway between the liquid and Ib capacitances, implying that the density was about halfway between the two phases. This is consistent with the fact that the Ia phase is metastable.

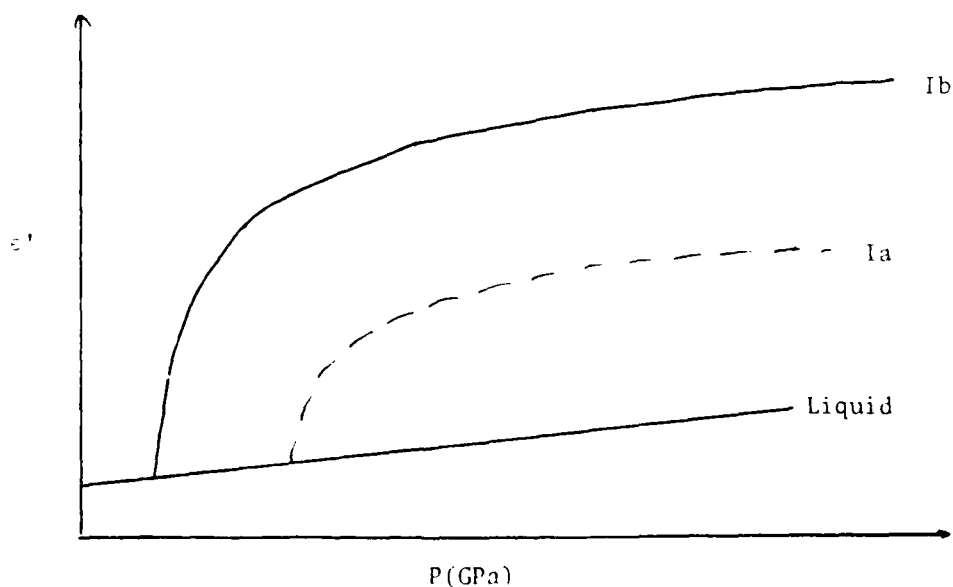


Figure 9. Schematic of the variation of the permittivity with pressure for various phases of  $\text{CCl}_4$ .

The fact that Bean's cells were able to form the Ia phase and the constant volume cells were not is quite significant. The probable reason comes from the design of the cells themselves. The cells from NBS were constant sample cells. No part of the sample liquid was required to flow through the cell. As a result, there was no internal agitation. The cells constructed in this paper were constant volume cells. The gap between the plates remained the same, but the density increased as more sample was forced between the plates. It may be that carbon tetrachloride forced through the cell is too agitated to solidify into the Ia phase.

A second possibility is that it is a sample volume effect. The constant volume cells contained about 10 times the amount of  $\text{CCl}_4$ . The absolute volume change upon freezing, then, is at least ten times as great. It is reasonable, then, that upon freezing the intermediate density phase (Ia) may be bypassed because of the dynamical aspects of the large absolute volume change of the large cell.

Morrison and Richards<sup>7</sup> have also suggested that the cell materials may be a factor. Further work concerning the Ia phase is necessary.

#### G. The Rhombohedral to Monoclinic Phase Transition

During the last data sequence for the sample of  $\text{CCl}_4$ , pressures were reached beyond the Ib-II phase transition. Previous transitions into the monoclinic phase had been avoided because the monoclinic phase is not plastic but is brittle.

This caution was found to be justified since the monoclinic phase destroyed the bellows as discovered after the data run.

The results of that data run are pictured in Figure 27. in Appendix I. The phase transition from the monoclinic phase is sharply contrasted to the rotator-liquid transition. Most importantly , the transition from the II phase is very sharp and exhibits no rounding features as seen in the rotator-liquid phase transitions. The II-Ib transition is more characteristic of the transitions in most crystals where a discontinuous change in volume occurs with little change in volume at other pressures.

## VII PRESSURE CALIBRATION

Finally, we consider the use of carbon tetrachloride for pressure calibration. Two possibilities for calibration are the liquid-to-rotator transition and the rotator-to-liquid transition.

The liquid-to-rotator phase transition offers a poor choice for use as a pressure calibration transition. As discussed in the Introduction, the phase transition must be well defined. The superpressing of carbon tetrachloride, however, provides no predictability as to when a transition will occur. Since shock waves can cause a transition independent of pressure, no fixed pressure can be attached to the transition. Hence, the liquid-to-solid transition cannot be used for calibration purposes.

Nevertheless, the rotator-to-liquid transition offers an excellent prospect for calibration purposes. Although the transition begins with a gradual expansion process, the final change into the liquid phase is characterized by a high rate of change of permittivity with respect to pressure. Furthermore, there is no hysteresis associated with this change and the melting processes are extremely well defined. The melting points found in this paper are reported in Figure 26, and are compared to the melting points reported by Bean and Wood<sup>2</sup>. Unfortunately, the melting points are temperature dependent. The temperature requirement, of course, is not an absolute requirement as described in the Introduction. But to make effective use of the rotator-to-



liquid transition, an accurate knowledge of the temperature is required, necessitating the use of a temperature bath.

Nevertheless, these studies have revealed a second technique which may prove useful in pressure determination. That is that the change of the dielectric constant with pressure for the liquid phase is an extremely reproducible phenomenon. This can be seen by the close agreement of the present work with that of Scaife<sup>3</sup> and Mopsik<sup>4</sup> as shown in Table 2. This has intriguing possibilities in these days of microprocessors since an automatic balancing, limited function bridge could be constructed which could convert the capacitive readings directly to pressure using software. Consequently, a digital pressure gage could be constructed using  $\text{CCl}_4$  as the capacitive transducer.

#### VIII. SUMMARY AND CONCLUSIONS

The permittivity of carbon tetrachloride has been studied as a function of pressure at various temperatures and thus has been studied in several phases. Several interesting results have been obtained:

1. Carbon tetrachloride superpresses readily and appears to be a normal extension of the liquid region. Since carbon tetrachloride transforms at any time from the superpressed region, a definite freezing point cannot be determined. For this reason, the liquid-to-rotator transition cannot be used as a pressure calibration point.
2. The rotator-to-liquid transition is well-defined and agrees with previously published values. The Ib-Liquid transition can thus be used for calibration purposes, but is temperature dependent requiring a knowledge of the temperature to get a pressure.
3. The low pressure portion of the Ib phase is very diffuse and is an intrinsic property of carbon tetrachloride. Four possible explanations are:
  - a. Mutual coexistence of liquid and solid,
  - b. Impurity effects,
  - c. Highly defective crystal structure, and
  - d. Expanding lattice spacings.
4. The compressibility of carbon tetrachloride becomes smaller with increasing pressure. At a phase transition, however, the lattice becomes very compressible.

## FOOTNOTES

1. P. W. Bridgman, Physical Review 3, 153 (1914).
2. V. E. Bean and S. D. Wood, Journal of Chemical Physics 72, 5838 (1980).
3. W. G. S. Scaife, Journal of Physics A: General Physics 4, 413 (1971).
4. F. I. Mopsik, Journal of Chemical Physics 50, 2559 (1969).
5. Smyth, C. P., Dielectric Behavior and Structure, New York: McGraw-Hill Inc., 1955, p.5.
6. Andeen, C., Fontanella, J., and Schuele, D., U.S.A.E.C. Contract No. 11-1-623, Technical Report No. 77, Nov. 1972.
7. J. A. Morrison and E. L. Richards, Journal of Chemical Thermodynamics 8, 1033 (1976).

## REFERENCES

1. Kittel, Charles. Introduction to Solid State Physics. New York: John Wiley and Sons, 1971.
2. Smyth, Charles Phelps. Dielectric Behavior and Structure. McGraw-Hill Book Co., Inc., 1955
3. Sherwood, John N., ed., The Plastically Crystalline State, New York: John Wiley and Sons, 1979.
4. Rao, C. N. R. and Rao, K. J., Phase Transitions in Solids, New York: McGraw-Hill Inc., 1978.
5. V. E. Bean and S. D. Wood, Journal of Chemical Physics 72 5838 (1980).
6. W. G. S. Scaife, Journal of Physics A: General Physics 4, 413 (1971).
7. F. I. Mopsik, Journal of Chemical Physics 50, 2559 (1969).

## APPENDIX 1

Figure 10: Permittivity of carbon tetrachloride at  $T=21.0^{\circ}\text{C}$

Figure 11: Permittivity of carbon tetrachloride at  $T=14.3^{\circ}\text{C}$

Figure 12: Permittivity of carbon tetrachloride at  $T=11.5^{\circ}\text{C}$

Figure 13: Permittivity of carbon tetrachloride at  $T= 1.9^{\circ}\text{C}$

Figure 14: Permittivity of carbon tetrachloride at  $T=-6.0^{\circ}\text{C}$

Figure 15: Permittivity of carbon tetrachloride at  $T=-13.4^{\circ}\text{C}$

Figure 16: Compressibility of carbon tetrachloride at  $T=21.0^{\circ}\text{C}$

Figure 17: Compressibility of carbon tetrachloride at  $T=14.3^{\circ}\text{C}$

Figure 18: Compressibility of carbon tetrachloride at  $T=11.5^{\circ}\text{C}$

Figure 19: Compressibility of carbon tetrachloride at  $T=11.5^{\circ}\text{C}$

Figure 20: Compressibility of carbon tetrachloride at  $T= 1.9^{\circ}\text{C}$

Figure 21: Compressibility of carbon tetrachloride at  $T=-6.0^{\circ}\text{C}$

Figure 22: Compressibility of carbon tetrachloride at  $T=-13.4^{\circ}\text{C}$

Figure 23: Capacitance readings for cyclohexane at  $T=35.5^{\circ}\text{C}$

Figure 24: Capacitance readings for cyclohexanol at  $T=-10.0^{\circ}\text{C}$

Figure 25: Compressibility of cyclohexane at  $T=35.5^{\circ}\text{C}$

Figure 26: Melting curve for the Ib-Liquid transition of  $\text{CCl}_4$ .

Figure 27: The monoclinic phase transition for carbon tetrachloride.

Figure 28: Argon calibration for the sample cell.

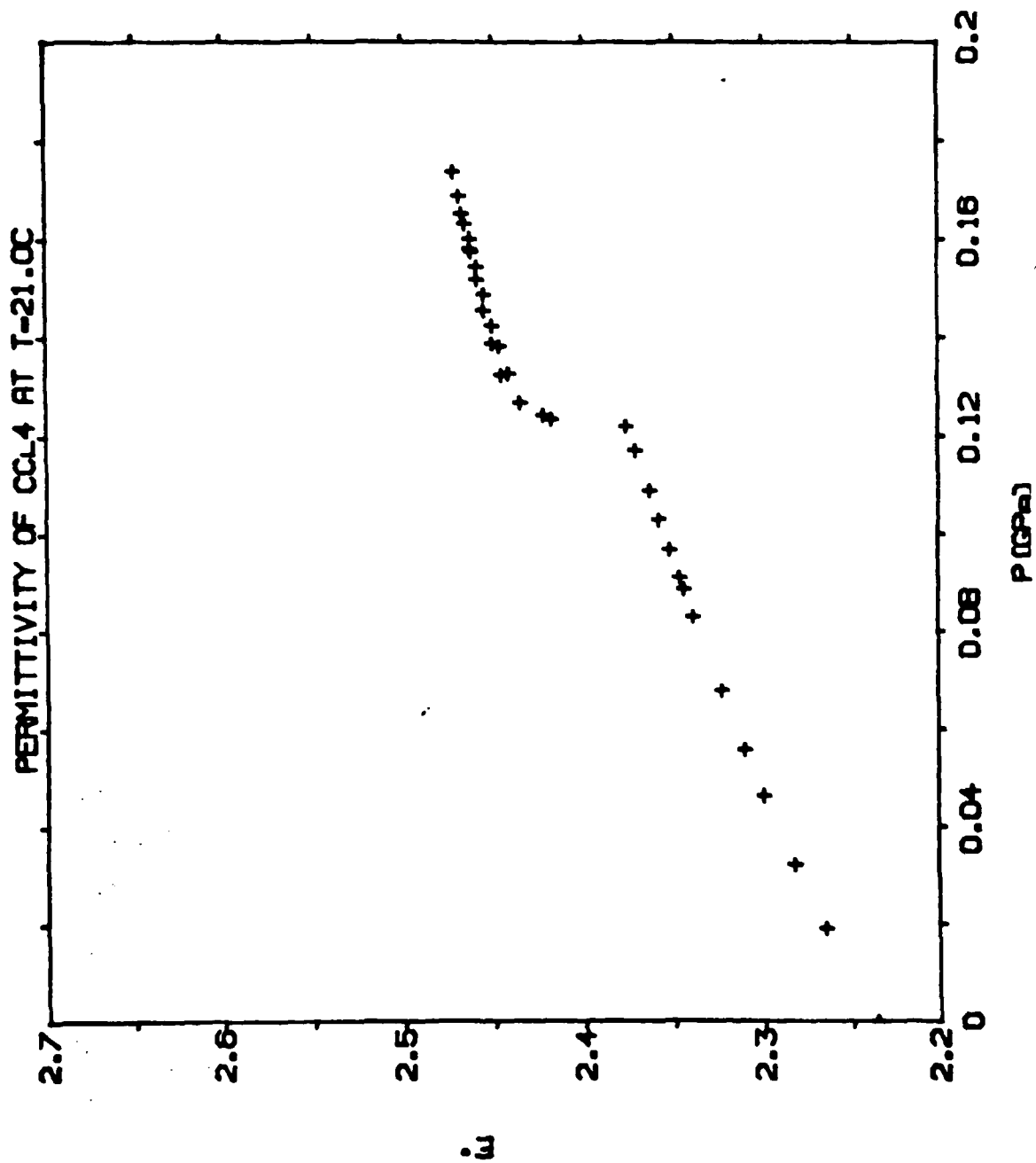


Figure 10: Permittivity of carbon tetrachloride at  $T=21.0^\circ\text{C}$

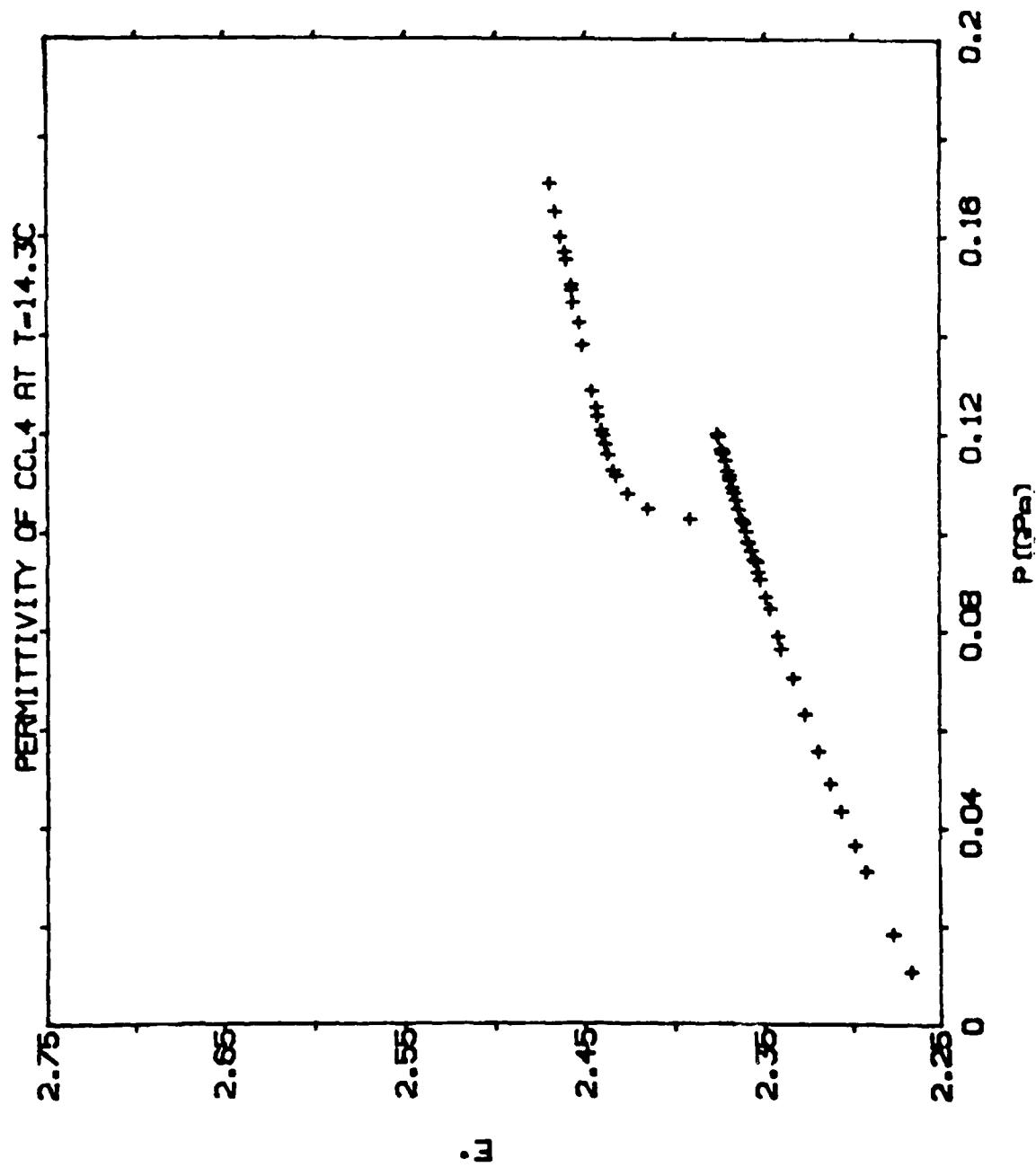


Figure 11: Permittivity of carbon tetrachloride at T=14.3°C

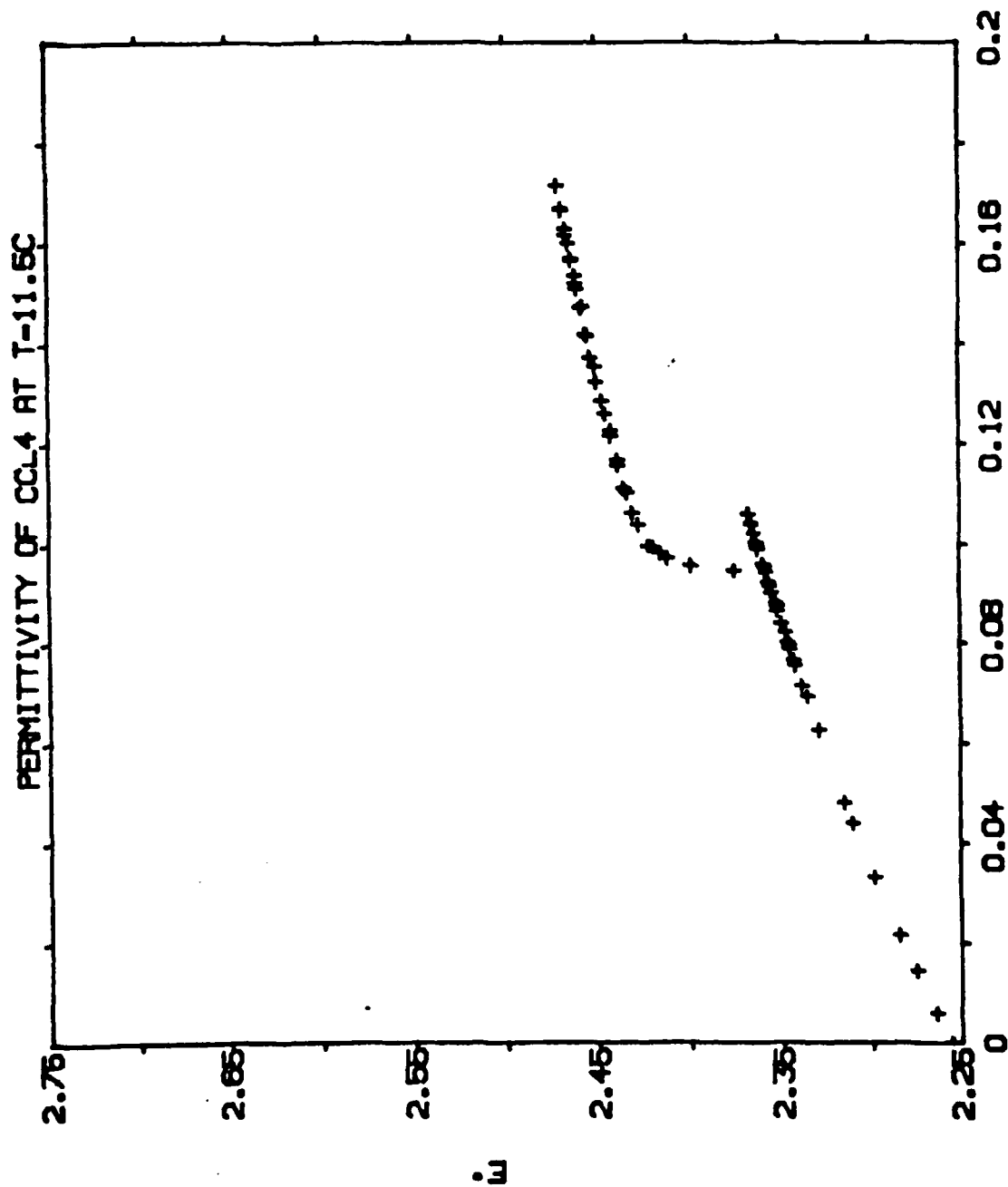


Figure 12: Permittivity of carbon tetrachloride at  $T=11.5^\circ\text{C}$



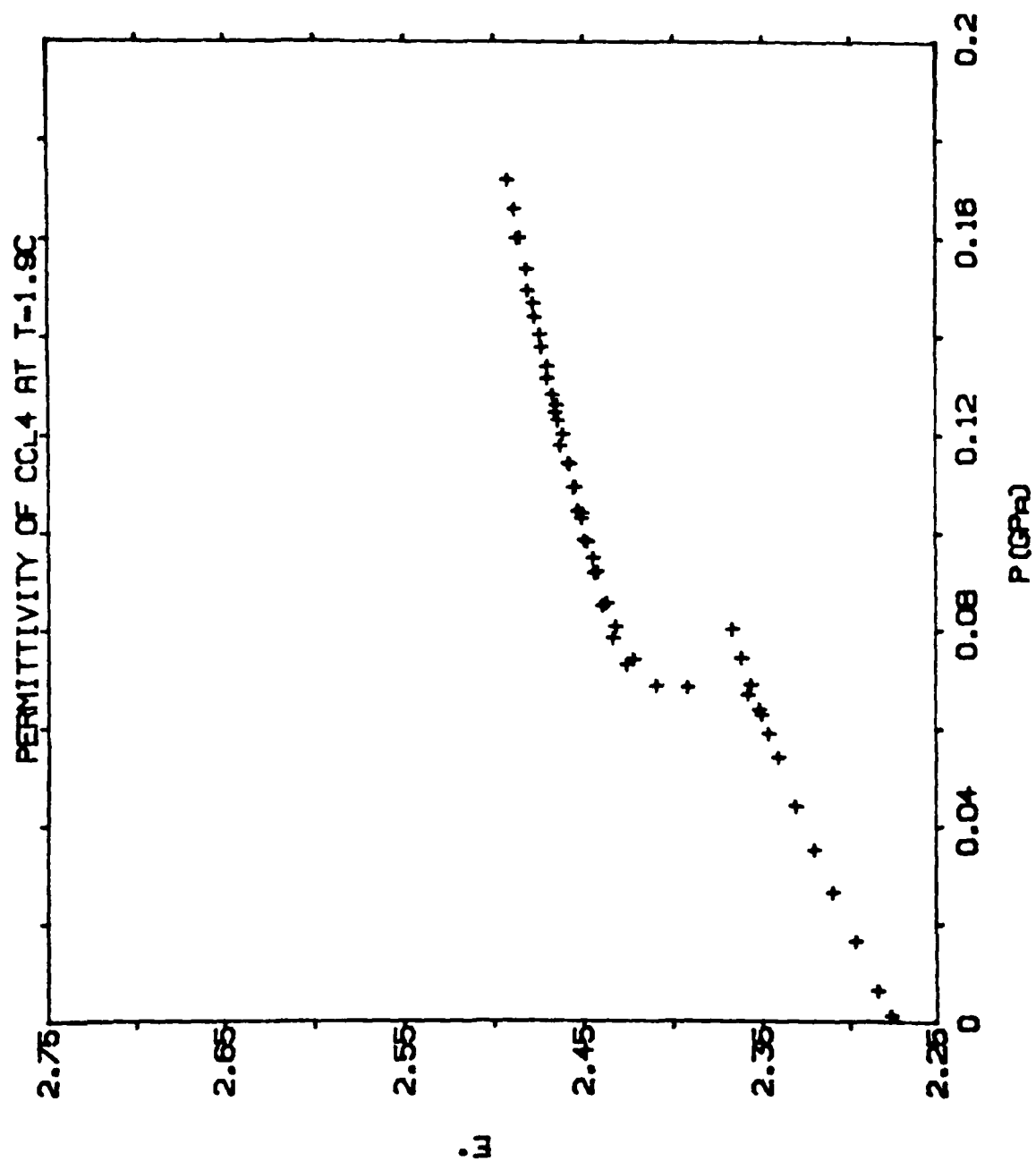


Figure 13: Permittivity of carbon tetrachloride at  $T=1.9^\circ\text{C}$

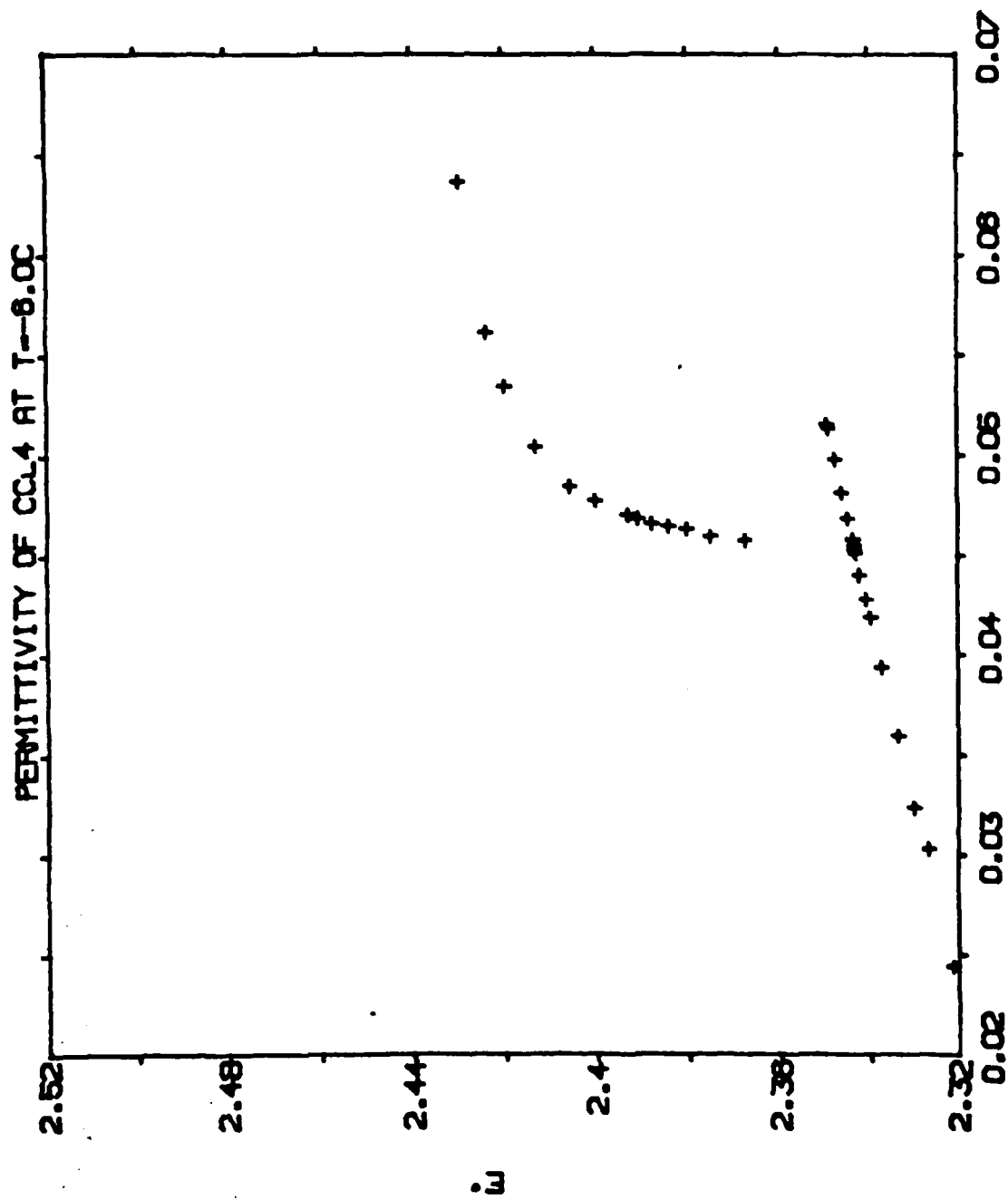


Figure 14: Permittivity of carbon tetrachloride at  $T = -6.0^\circ\text{C}$

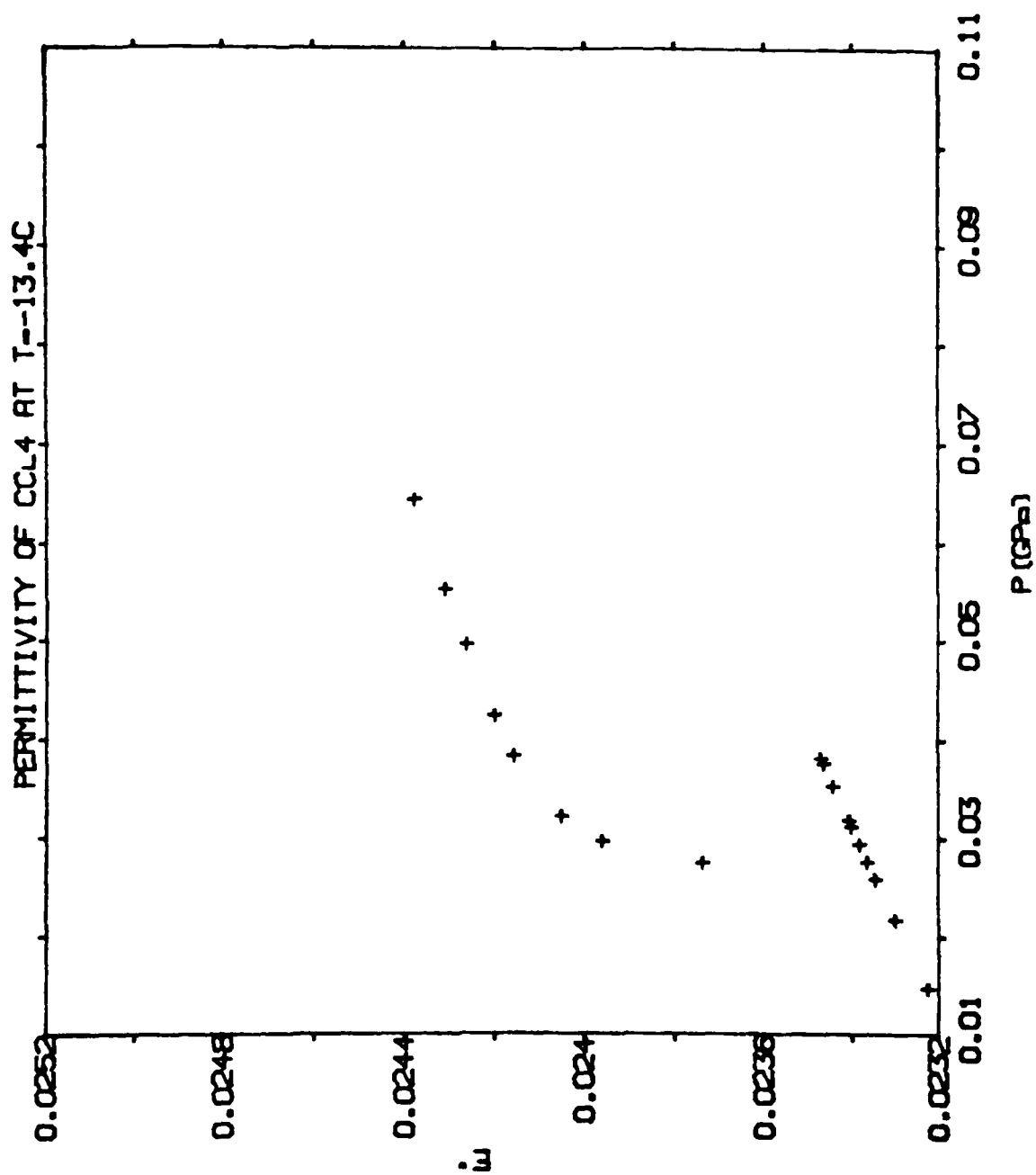


Figure 15: Permittivity of carbon tetrachloride at T = -13.4°C.

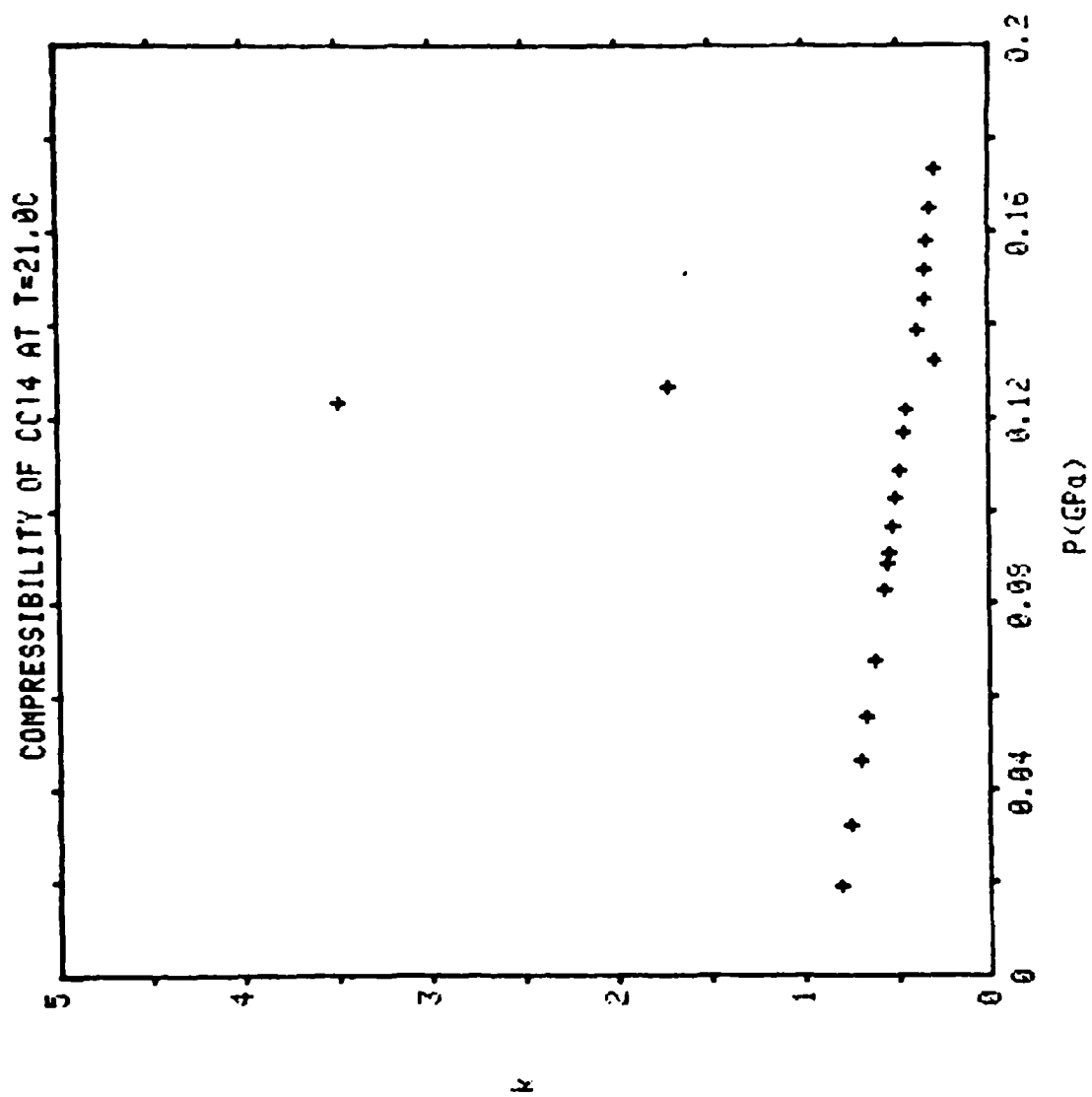


Figure 16: Compressibility of carbon tetrachloride at  $T=21.0^\circ\text{C}$

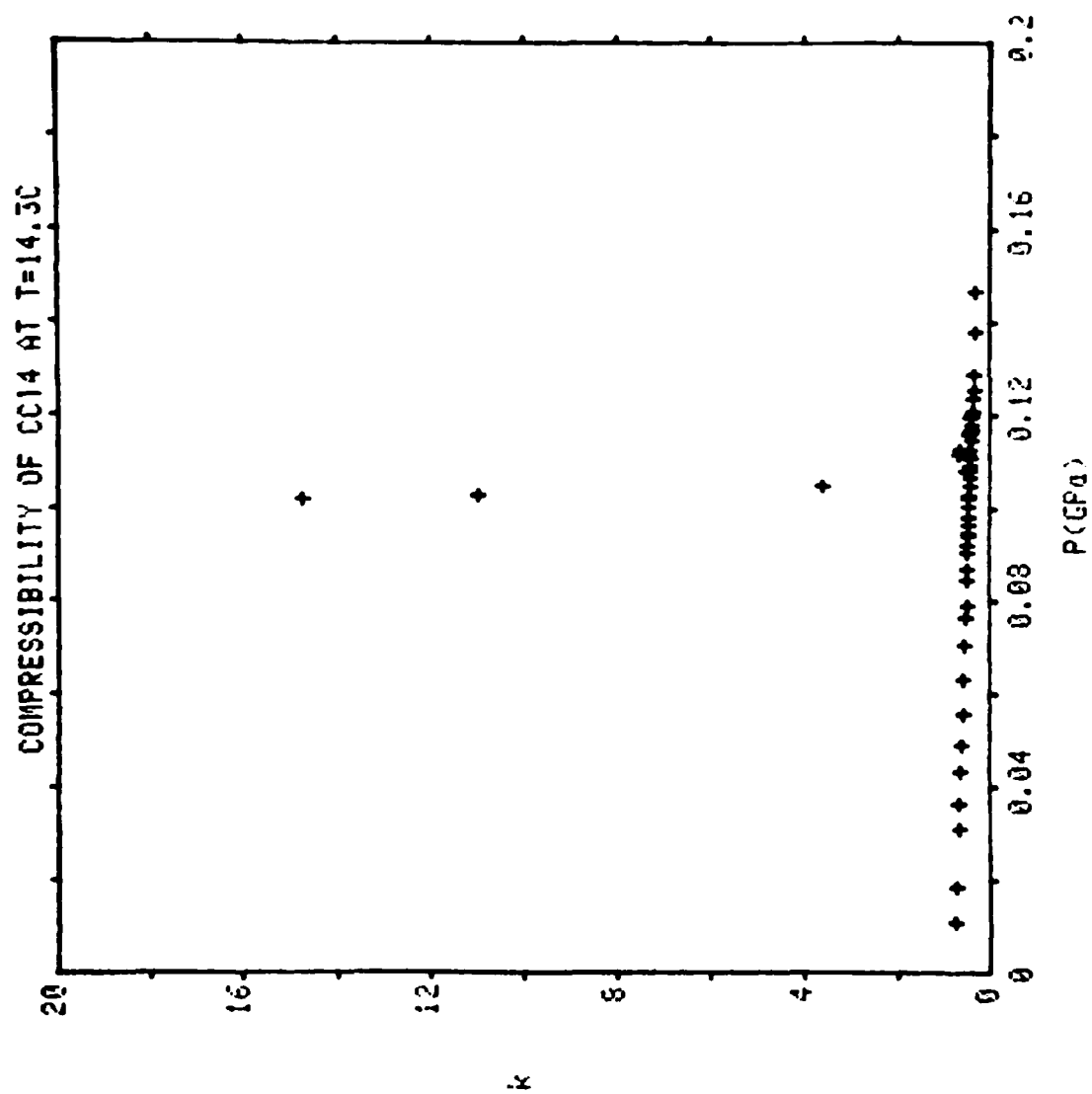


Figure 17: Compressibility of carbon tetrachloride at T=14.3°C

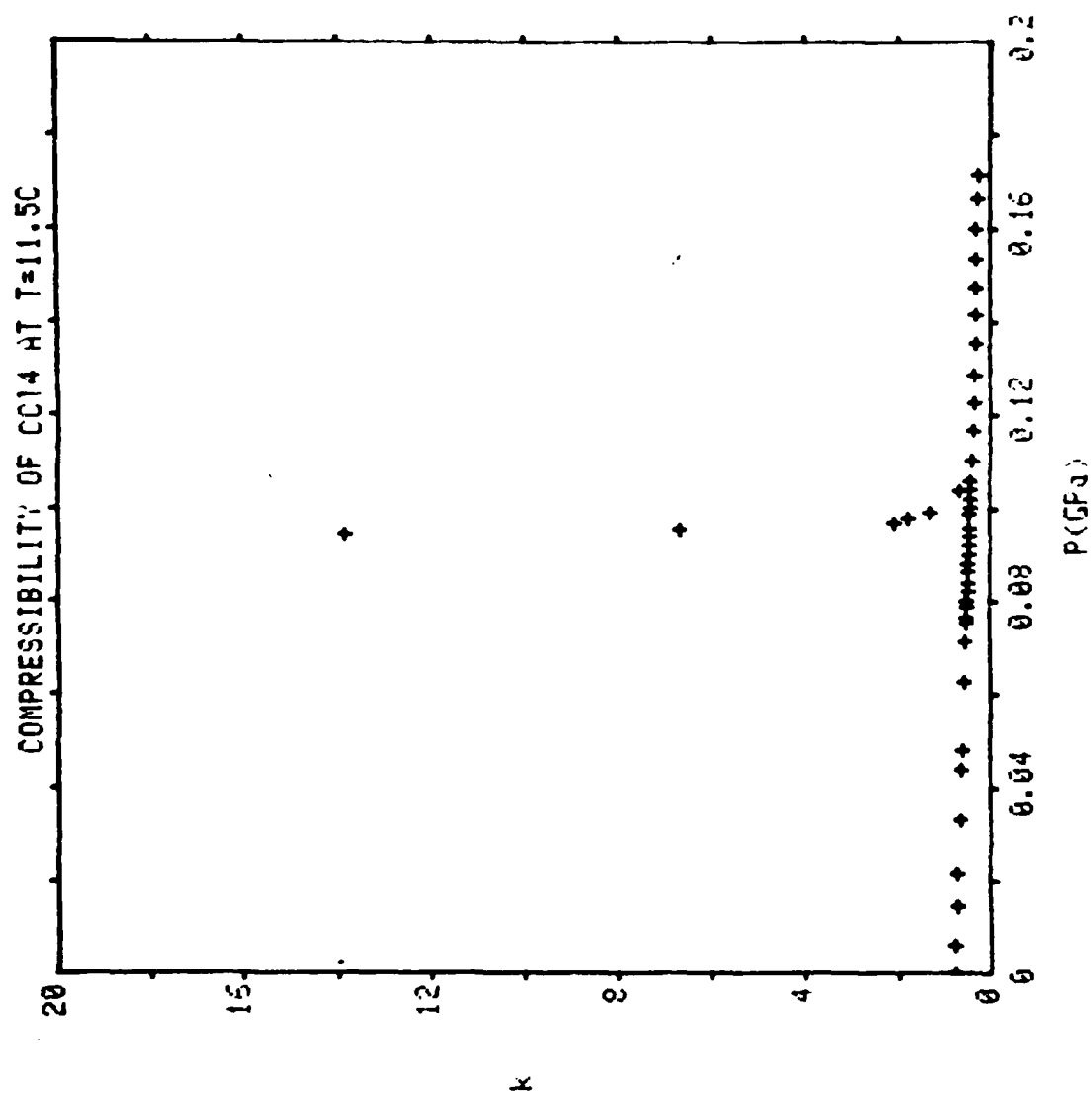


Figure 18: Compressibility of carbon tetrachloride at  $T=11.5^\circ\text{C}$

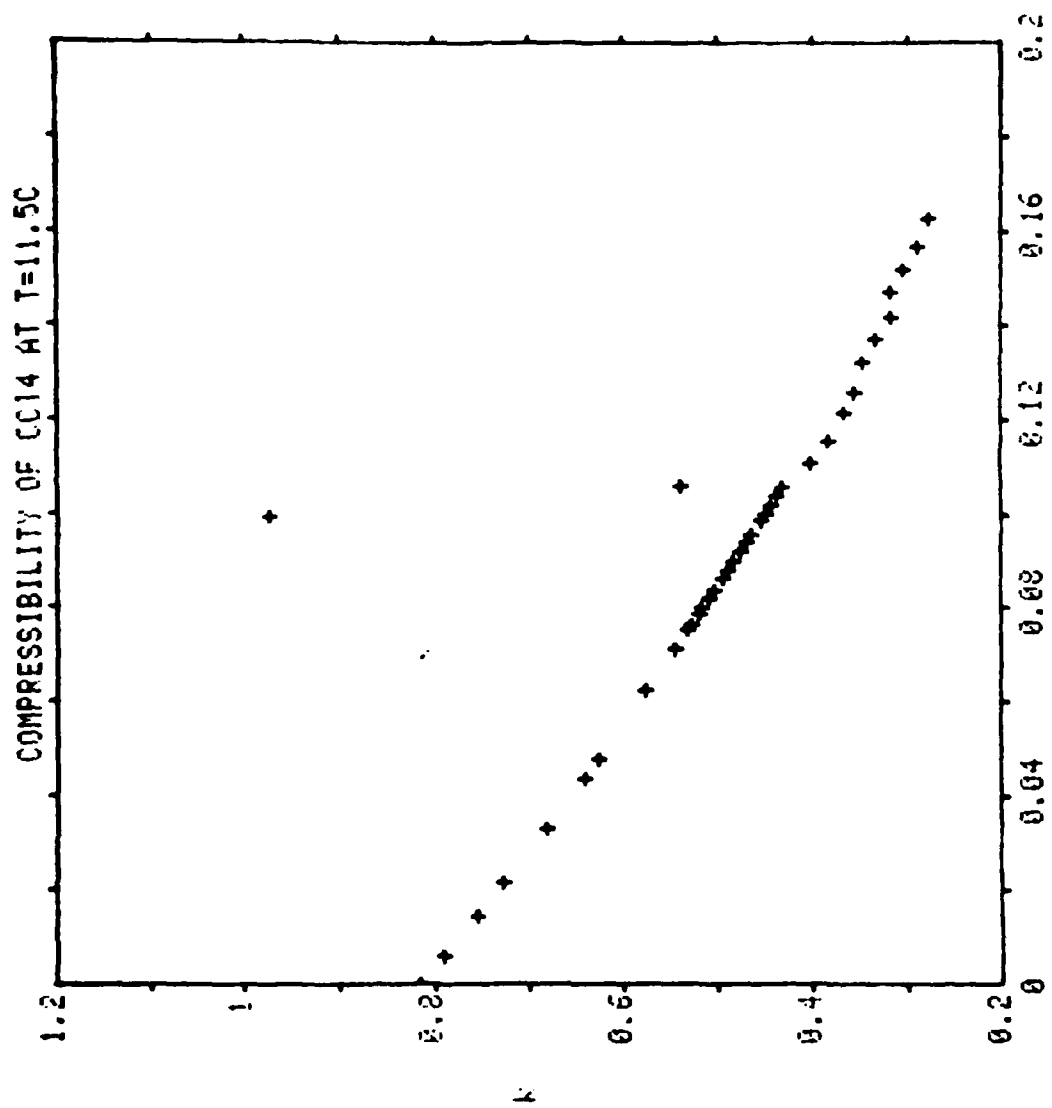


Figure 19: Compressibility of carbon tetrachloride at  $T=11.5^\circ\text{C}$

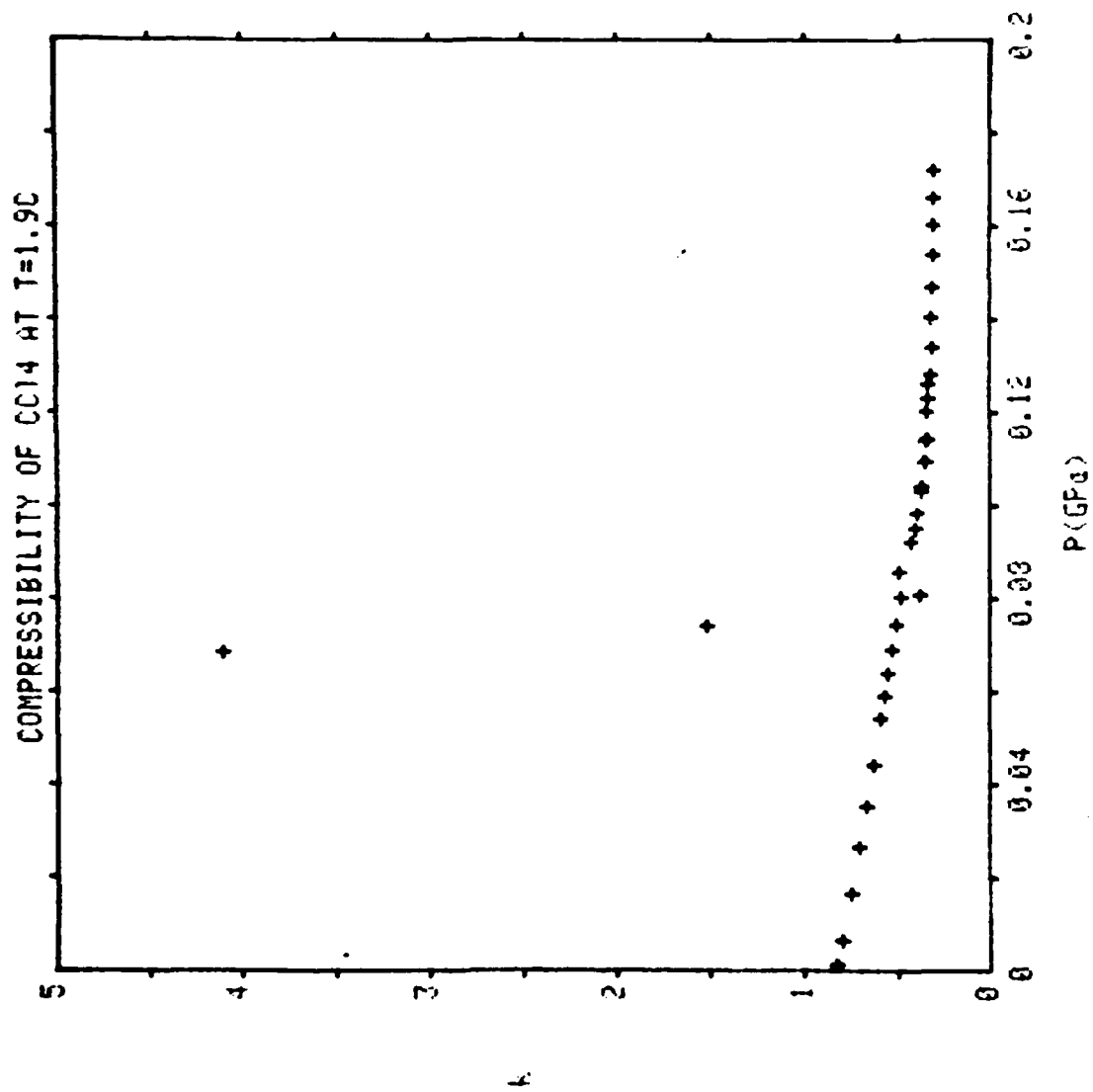
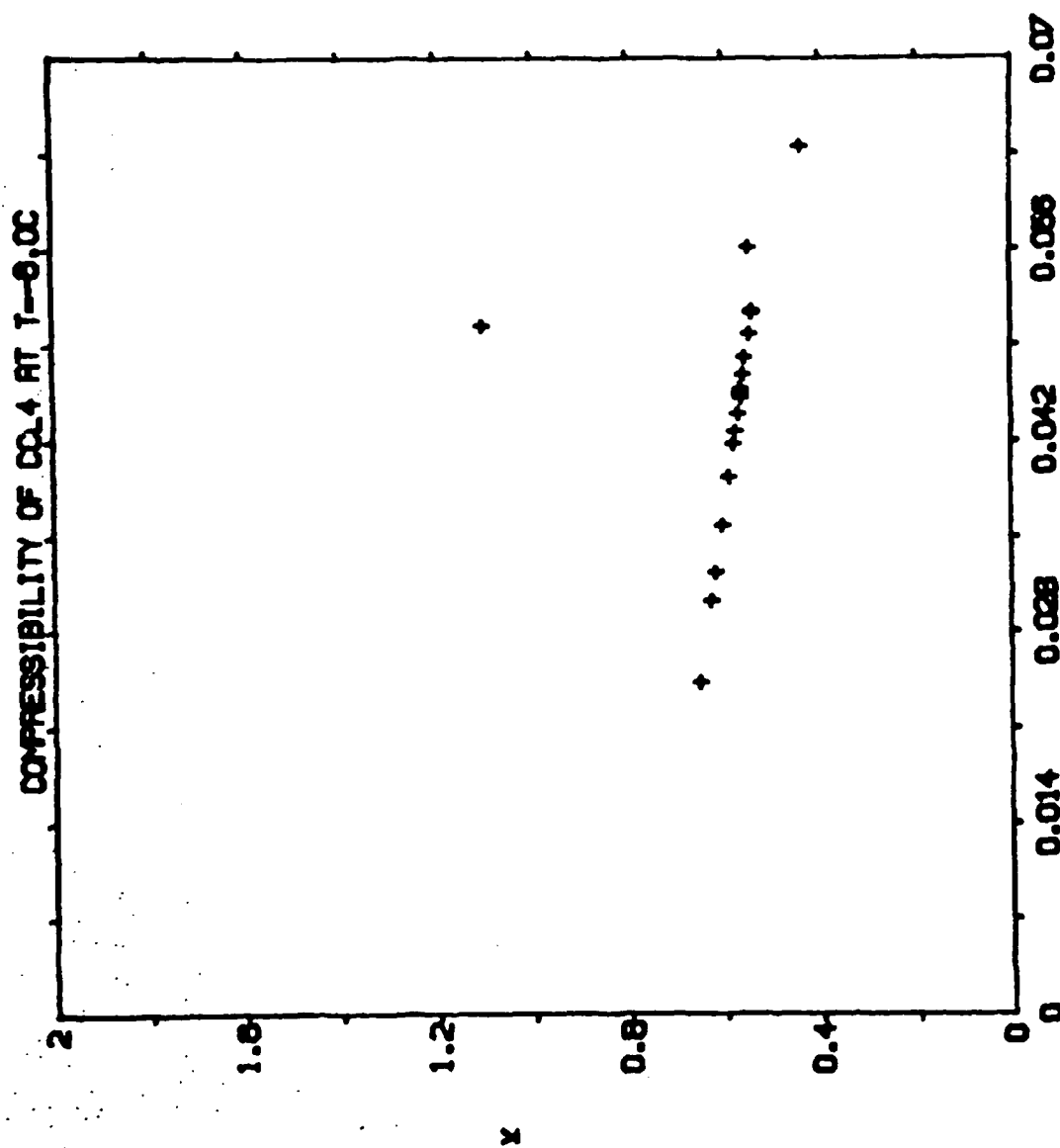


Figure 20: Compressibility of carbon tetrachloride at  $T=1.9^\circ\text{C}$





**Figure 21:** Compressibility of carbon tetrachloride at  $T = -6.0^{\circ}\text{C}$

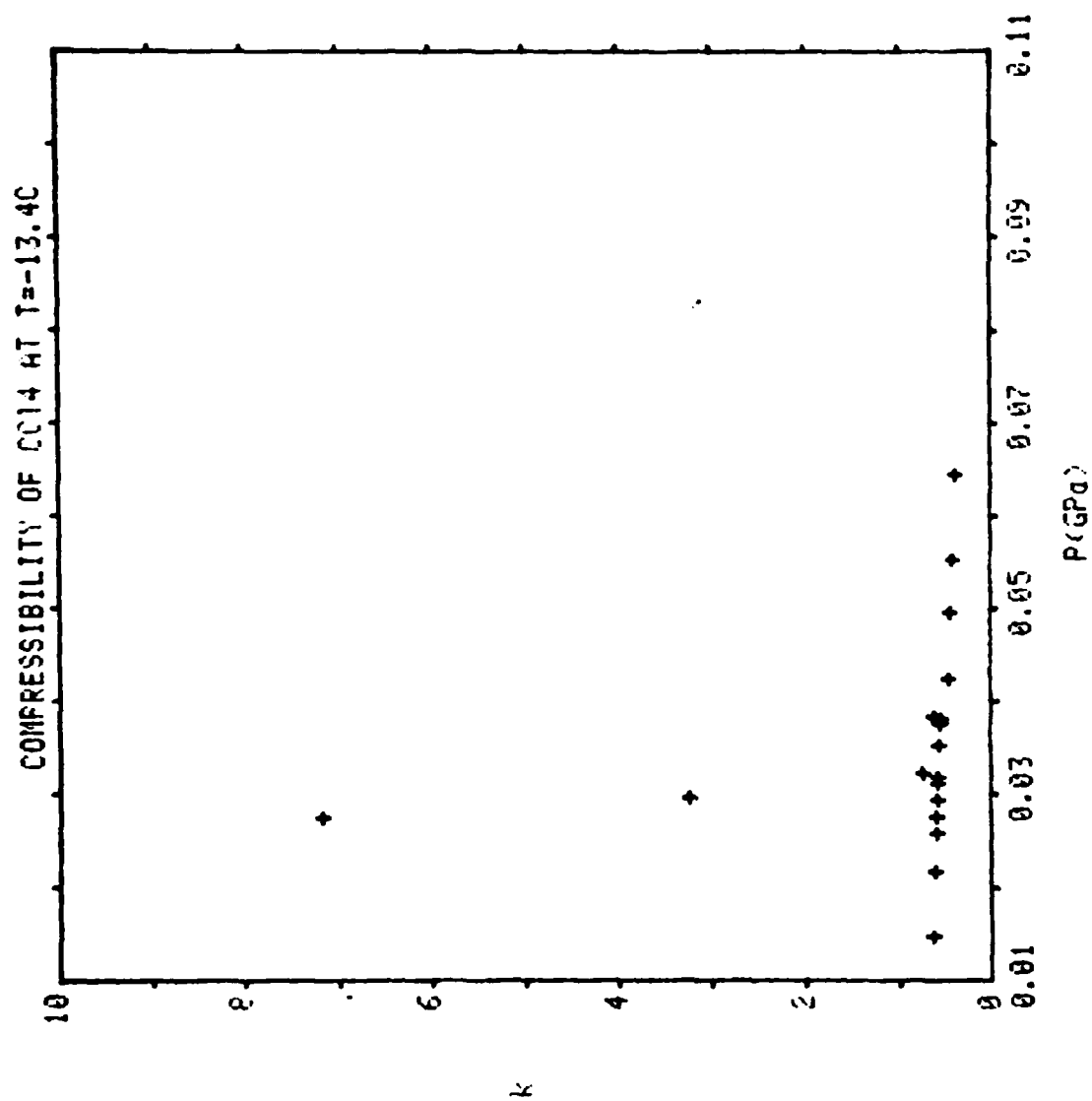


Figure 22: Compressibility of carbon tetrachloride at T = -13.4°C

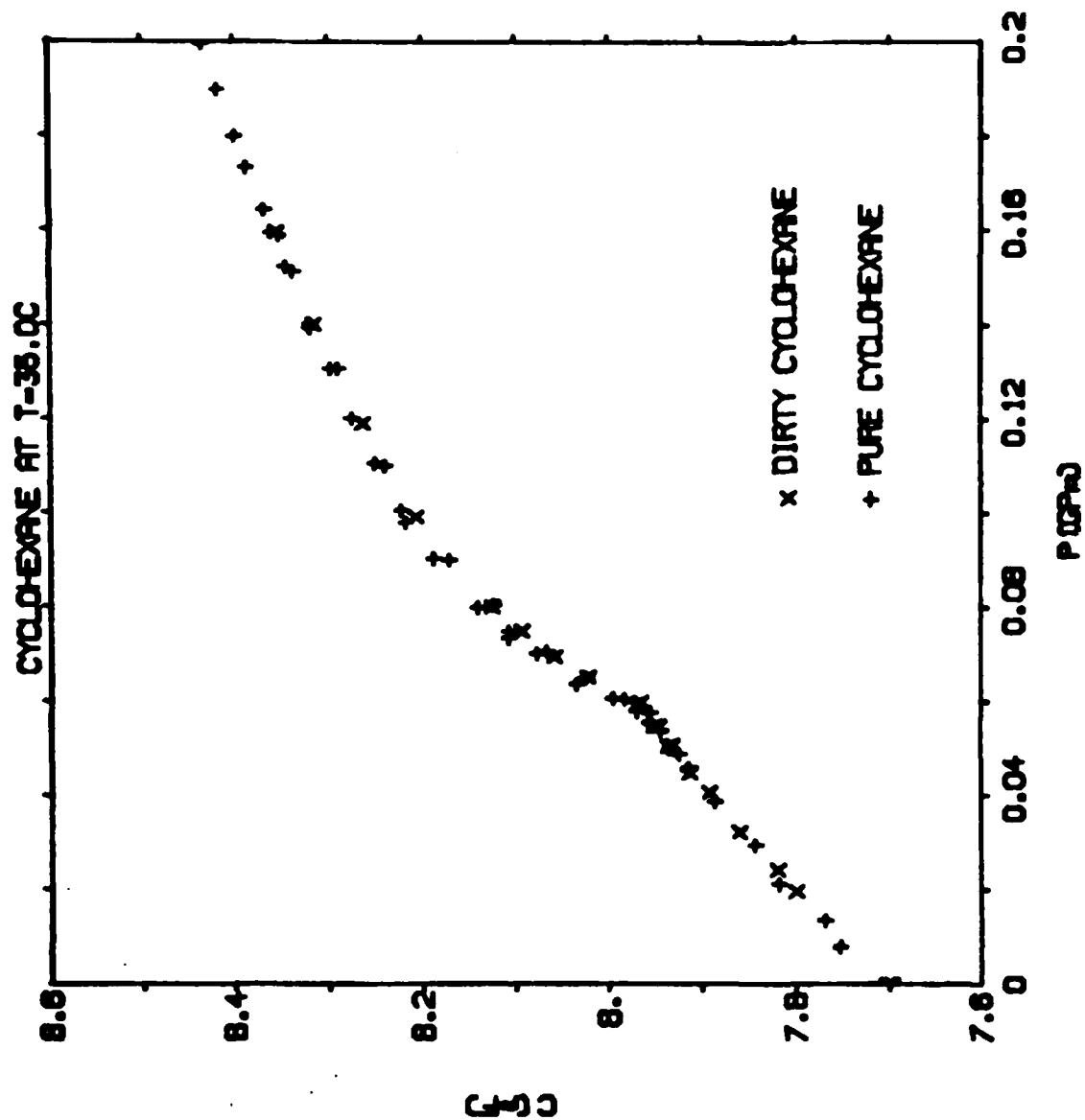


Figure 25: Capacitive readings of cyclohexane at T=35.0°C

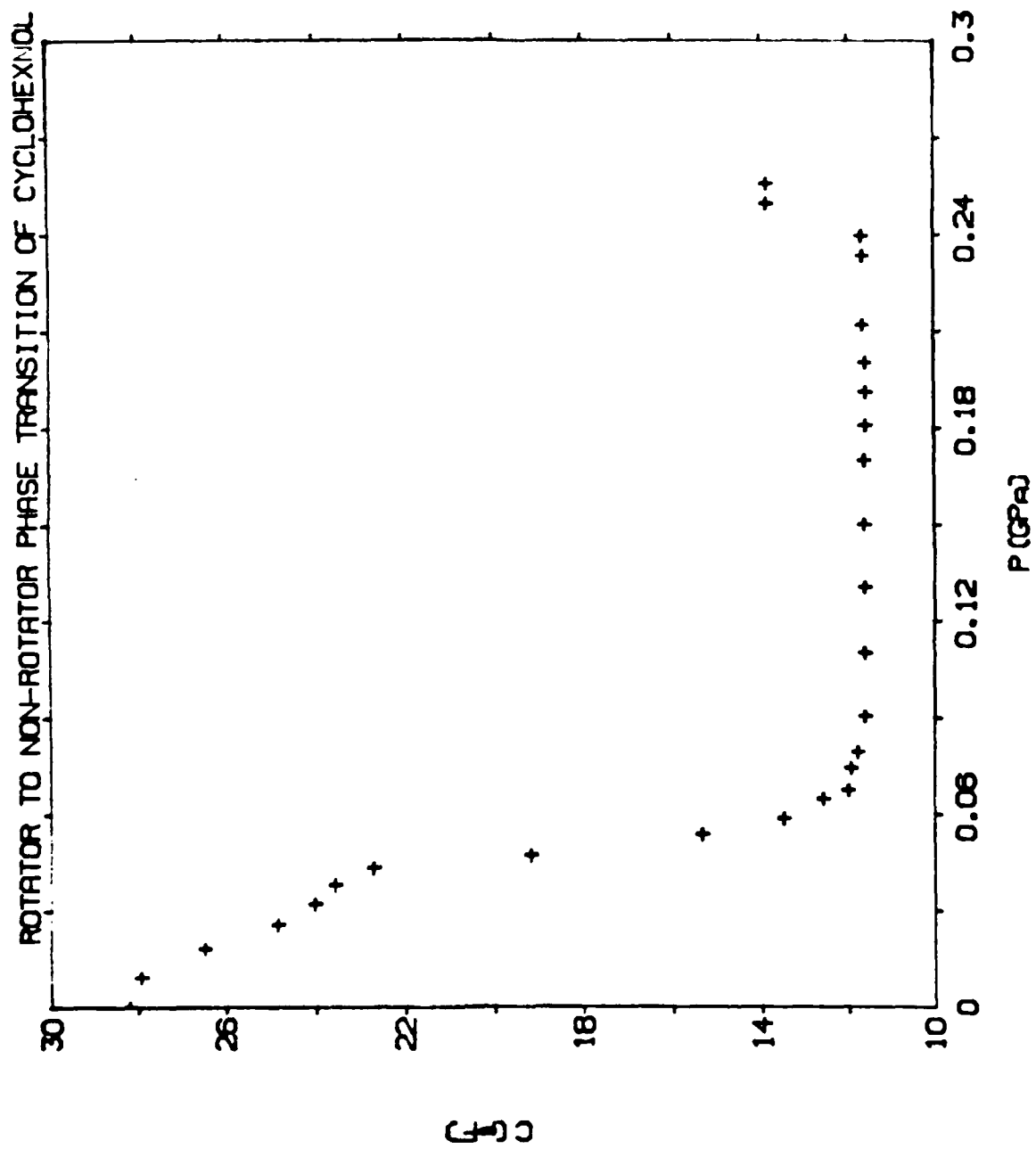


Figure 24: Capacitance readings for cyclohexanol at  $T = -10.0^{\circ}\text{C}$

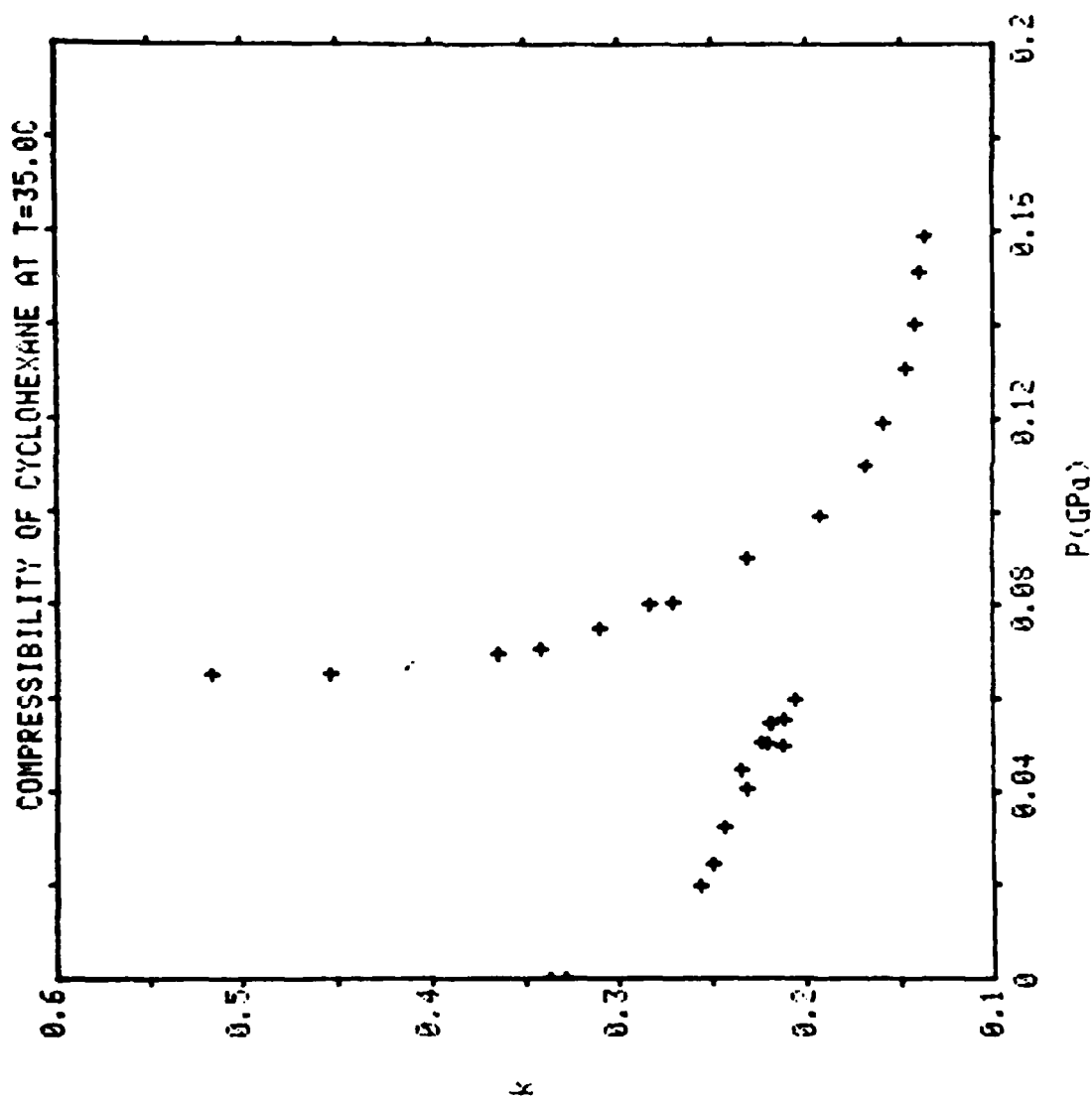


Figure 25: Compressibility of cyclohexane at  $T=35.0^\circ\text{C}$

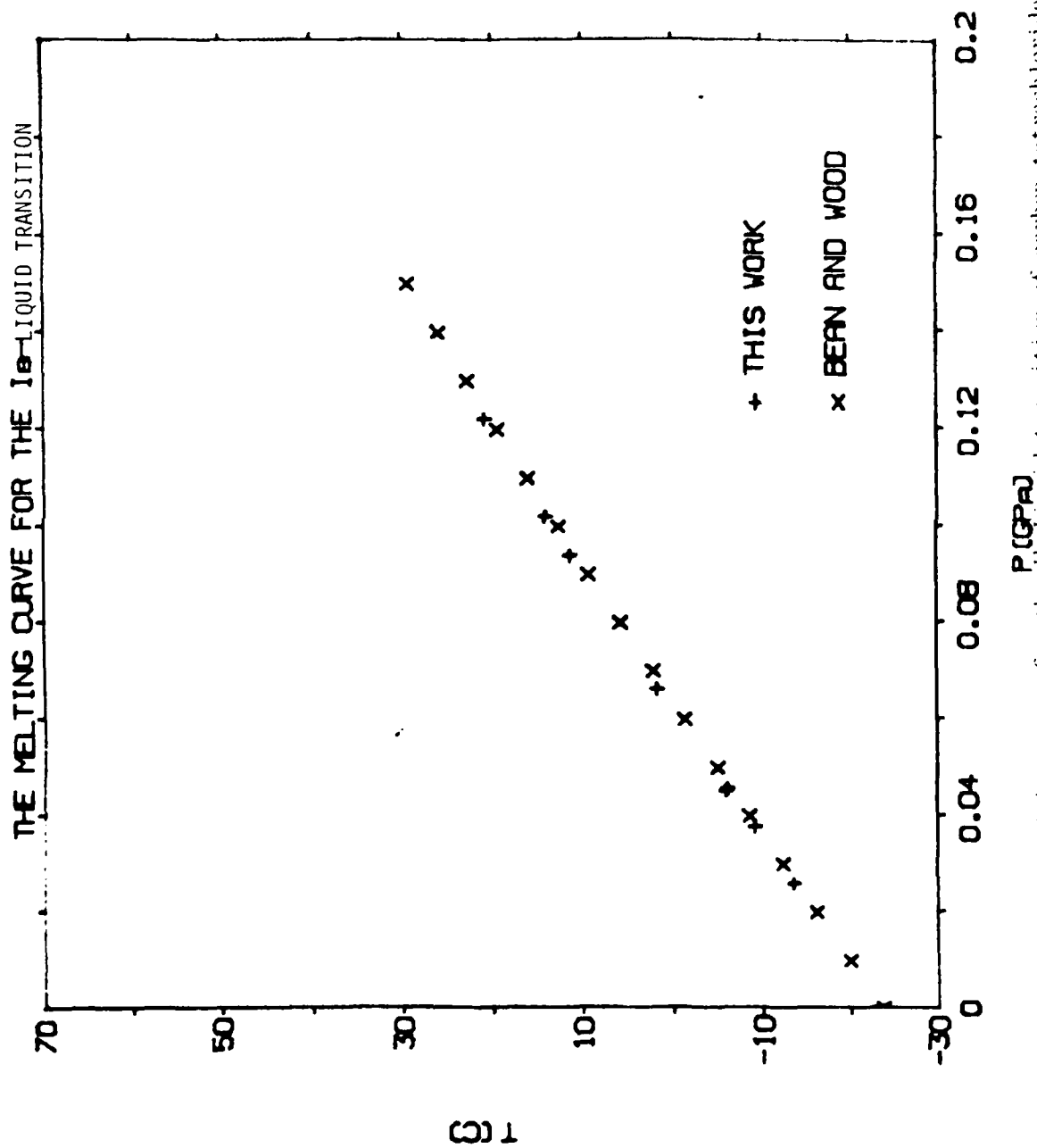


Figure 26: Melting curve for the I<sub>B</sub>-Liquid transition of carbon tetrachloride

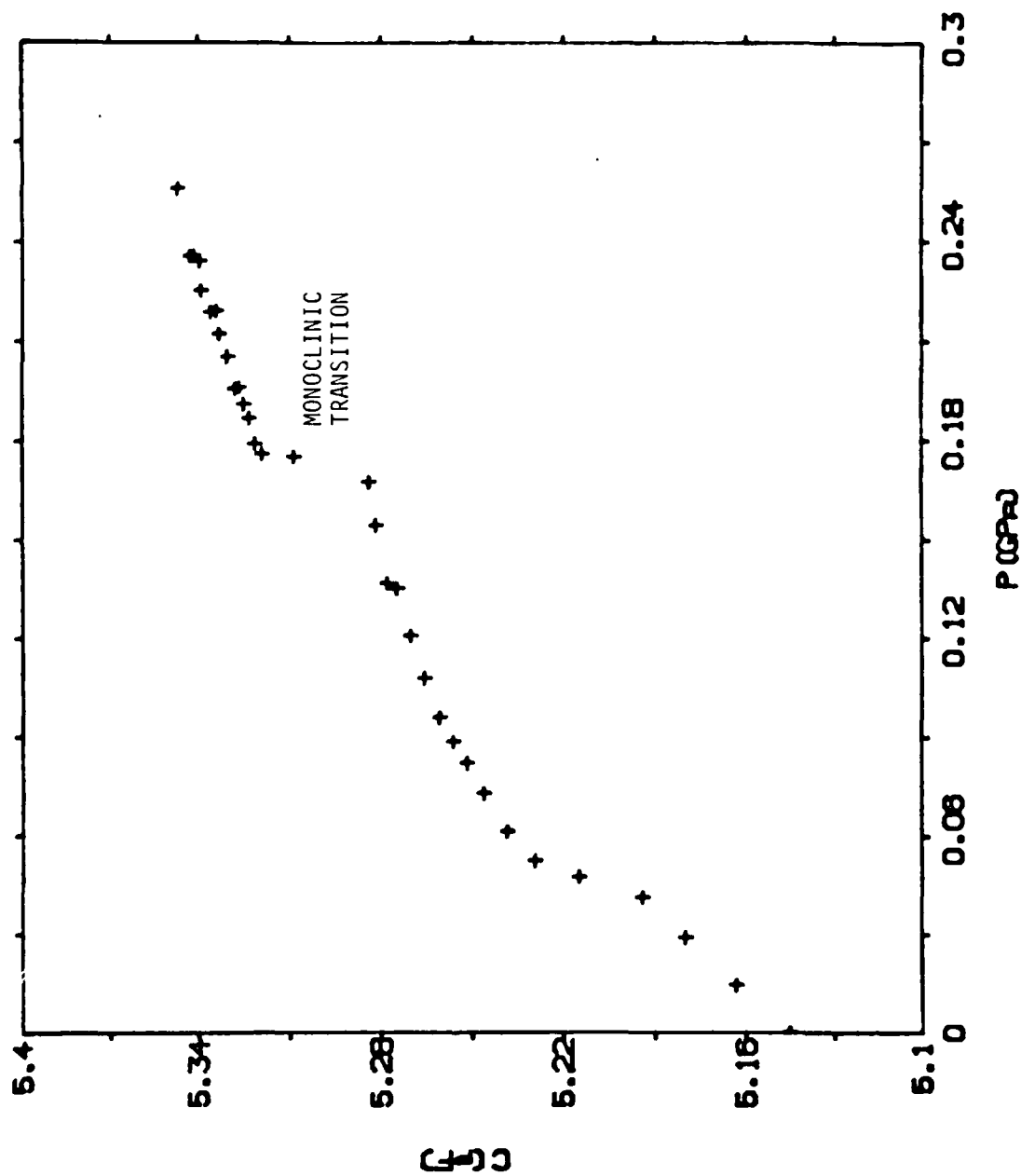


Figure 27: The monoclinic phase transition for carbon tetrachloride at  $T = -10.0^{\circ}\text{C}$

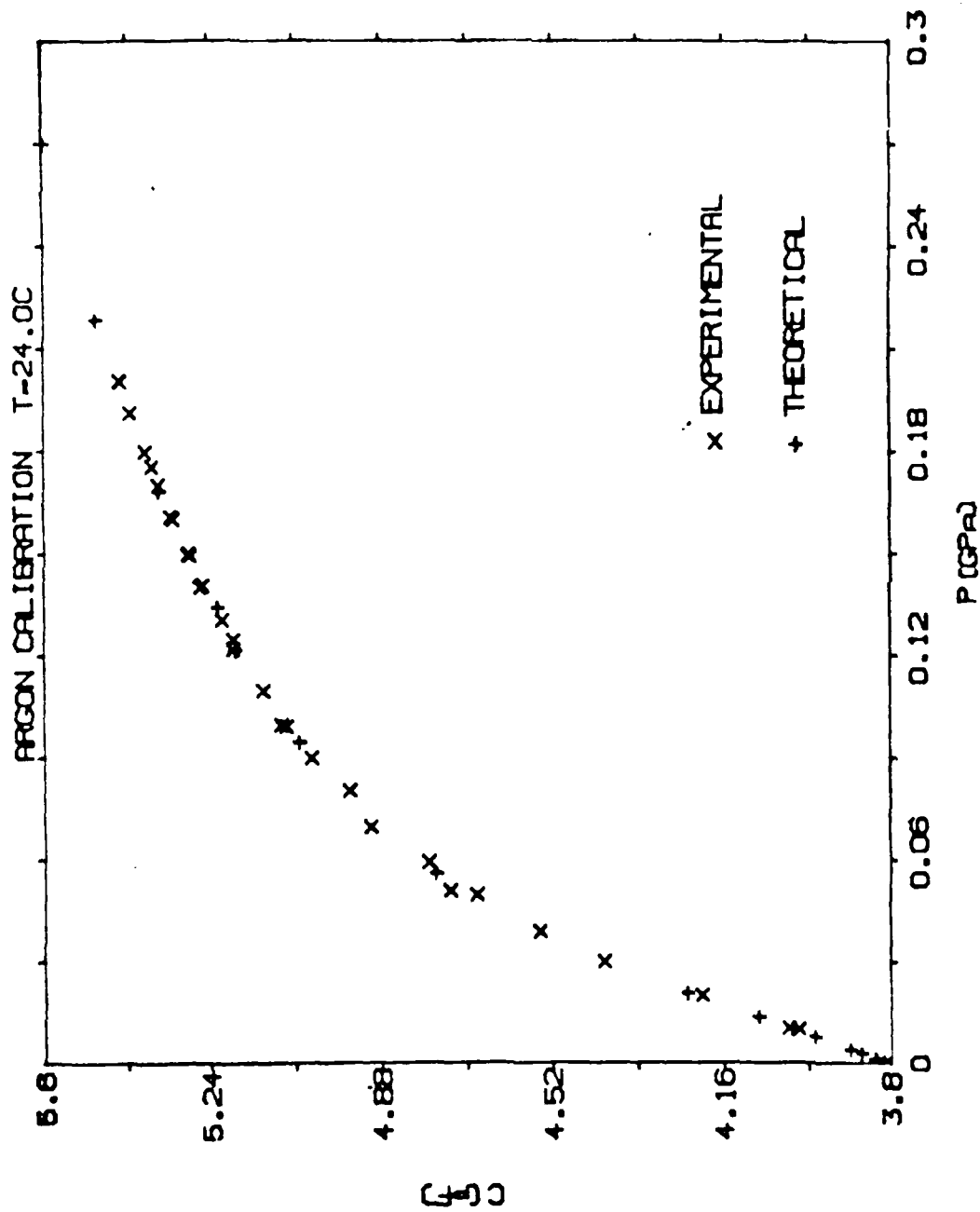
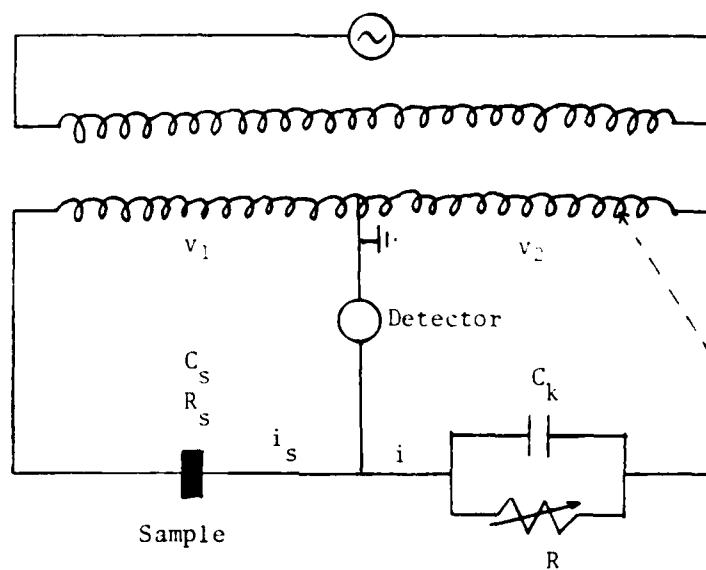


Figure 28: Argon calibration for the sample cell.



## APPENDIX II

## THE CAPACITANCE BRIDGE



The capacitance bridge balances the values of a known capacitance and potential with that of the sample to determine the capacitance of the sample.  $V_1$  and  $C_k$  are known constants.  $V_2$  and  $R$  are known variables. For the capacitance measurements:

$$V_1 = \frac{i_s}{\omega C_s}$$

$$V_2 = \frac{i}{\omega C_k}$$

$V_2$  is adjusted until  $i_s = i$ , at which point no current flows through the detector. When balanced in this manner,

$$\frac{V_1}{V_2} = \frac{1/C_s}{1/C_k} = \frac{C_k}{C_s}$$

$$C_s = \frac{V_2}{V_1} C_k$$

For the conductance measurement,

$$V_1 = i_s R_s$$

$$V_2 = iR$$

When balanced ( $i_s = i$ ),

$$R_s = \frac{V_1}{V_2} R$$

G is simply the reciprocal of  $R_s$ .

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